PHYSICO-CHEMICAL AND TRACE ELEMENT STUDIES ON CLAYS AND SOILS

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CHAPTER I

GENERAL INTRODUCTION

Soil: An Introduction

Soil, like faith, is the substance of things hoped for, the evidence of things not seen. Some two and a half billion people depend on it for food and clothing. And, by and large, it never fails. Here and there, because of ignorance and inefficiency, coupled with war and pestilence, a few millions may starve, and other millions may go to bed hungry more or less regularly. The productive capacity of the land as a whole, however, is far greater than is required to feed all the people on earth.

Nevertheless, the Malthusian principle that population is kept under control by famine, pestilence, and war still applies over a large part of the earth. It remains to be determined whether this principle can be permanently set aside by man through the application of the sciences at his command.

Man seems to have taken to agriculture in prehistoric times. Ancient carvings in caves and similar other dwellings show that they practiced agriculture about 3000 B.C. The ancient Hebrews left the art of growing crops about 300 B.C. and the Romans attained a very high standard in the pursuit of agriculture before the Christian era.

In India the art of agriculture has reached as high a state as, if not greater than, in Europe in ancient times. By Vedic period, the general principles of various agricultural operations such as ploughing, sowing, irrigation, etc., and of plant nutrition had been well understood. A system of cooperative farming seems to have been in vogue in those times.

During the sixteenth and seventeenth centuries, when people began taking more interest in the study of science in Europe, attempts were made to apply the knowledge of physical science, especially chemistry, to the improvement of agriculture. The remarkable discoveries made in the realm of natural science were then, for the first time, applied to agriculture.

Davy in England and Schubler in Germany recognised the importance of physical properties of soils in plant growth, especially their relation to water, air and heat. In the latter half of the nineteenth century, Wollny in Germany, King and Hilgard in America further extended these studies in an attempt to unravel the relation between physical properties of soil and crop production.

The problem of soil fertility took a new turn with the study of the colloidal nature of soil at the end of the last and the beginning of the present century. The revelation that soil colloidal particles were naturally crystalline in structure and carried by virtue of their large surface area, the role of this constituent in the maintenance of soil fertility.

Fast f r, the knowledge of the chemical, physical and biological behaviour of the soil was obtained mainly from the utilitarian point of view, viz., for obtaining bigger and better crops. When it was recognised as a basic science, a branch of agriculture and it remained as a handmaid of other sciences. Though the ultimate justification for soil research was to devise ways and means to improve the soil conditions that increased crop yields it was realised that many problems in soil science must be studied without any direct reference to that aspect. This new approach has now made great strides in unfolding the intricacies of soil behaviour and plant nutrition, and in elucidating several phases of soil problems not only of fundamental but also of practical value.

Soil may be defined as a natural body of mineral and organic constituents differentiated into horizons which differ among themselves as well as from the underlying material in morphology, physical make up, chemical composition, and biological characteristics. It is a three dimensional dynamic, natural body, occurring on the surface of the earth.

Broadly speaking soil consists of four components namely, mineral material, organic matter, water and air, all present in a fine state of sub-division and intimately mixed. Humus or the matter in one of the five components of the soil. It occurs normally in the form of amorphous dark coloured product formed by the intermixing of plant and animal materials. The product besides being responsible for its fertility, gives

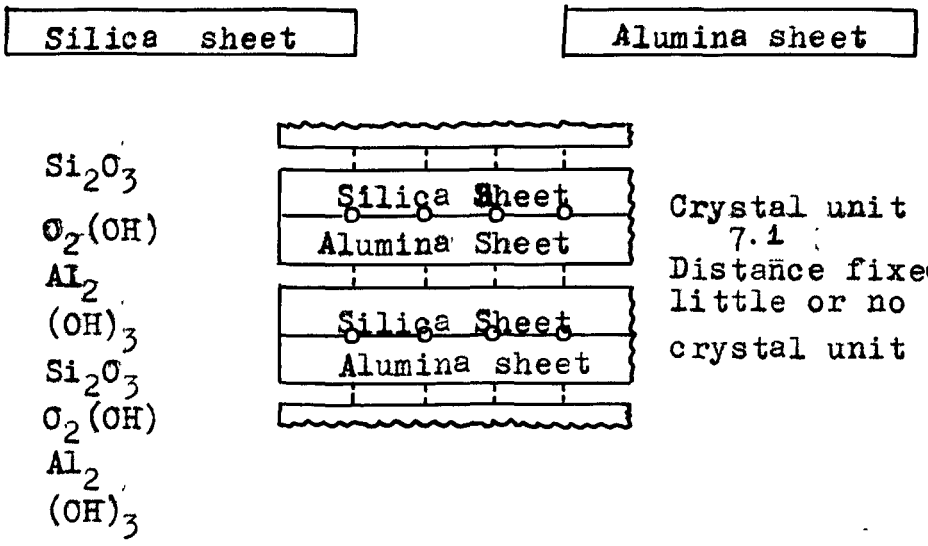
the soil its acidic and colloidal properties. And then we have the most important and yet highly intriguing constituent, the mineral matter, to which most of the complexities associated with soil investigations are attributed.

The mineral matter consists of particles of varying sizes, those in the finer states of sub-division (< 0.002 mm) forming the clay fraction while the coarse fraction consists mainly of rock debris. The clay fraction is specially important because it confers colloidal properties on the soils and controls its many properties. Its chemical constituents are silica, alumina and water together with small quantities of iron, alkalis and alkaline earths. In tropical climates, iron and aluminium hydroxides make up an appreciable amount, sometimes the greater part of the clay fraction. The older concept that clay particles are more or less spherical has now been replaced by a newer one.[1] It is now well established that the particles are laminated, that is, made up of layers of plates or flakes, the individual sizes and shape depending upon their mineralogical organization and the conditions in which they have developed, e.g., hexagonal blades, rods or fluffy.

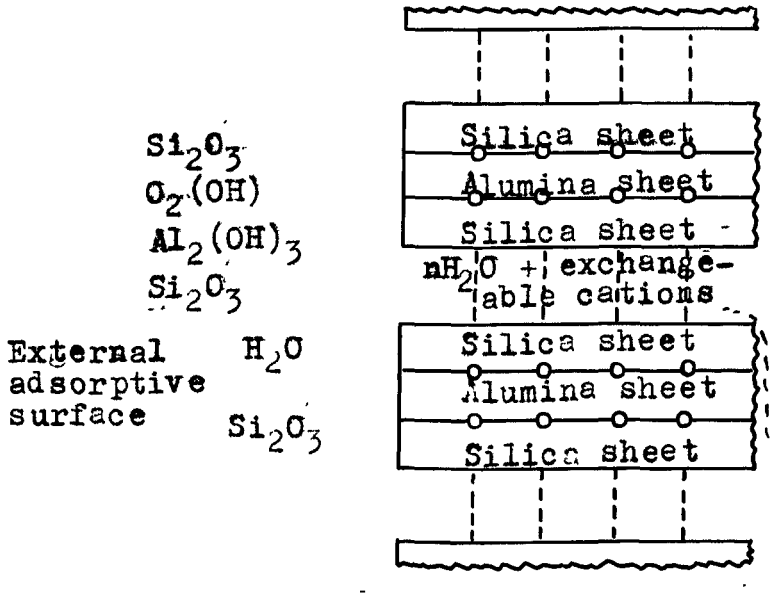
Extensive studies by x-ray diffraction patterns[2-3] and other methods like electron microscopy[4], I-R[5], D.T.A. etc., have shown that clays are crystalline in nature and are composed of single building units with definite spacial arrangements in the crystal lattice. The single building sheet of the clay mineral are two dimensional arrays of silicon-

oxygen tetrahedra and two dimensional arrays of aluminium or magnesium-oxygen-hydroxyl octahedra. In clay minerals such sheets of tetrahedra and octahedra are superimposed in different fashions. The difference in the properties of various clays is now believed to depend on the special arrangement of these units in the crystal lattice. The structure of the common clay minerals have been determined in considerable detail by numerous investigators based on the generalisations of Pauling.[6] Two structural units are involved in the atomic lattice of most of the clay minerals. The first consists of a silicon tetrahedron in which a silicon atom is equidistant from four oxygens or hydroxyls if needed to balance the structure, the silicon being in the centre (O-O distance 2.55A°; unit thickness 4.93A°). The second unit consists of two sheets of closely packed oxygen or hydroxyls in which Al, Fe or Mg atoms are embedded in octahedral coordination so that they are equidistant from six oxygen or six hydroxyls (O-O distance 2.50A°; OH-OH distance 2.94A°; unit thickness 5.05A°). Combination of these structural units (held by chemical forces) with modifications, finally give rise to structure of the clay minerals that are found in the colloid clay fractions of soils (vide figure 2)

Generally speaking, three groups of clay minerals are distributed in nature although a few less familiar ones are also known to exist. These are (i) kaolinite (ii) montmorillonite and (iii) illite.



1 (a) Diagramatic edge view of kaolinite showing two complete layers, the respective crystal units are bound to eatch other tightly by an oxygen-hydroxyl linkage, thereby giving a restricted and non-expending lattice, the adsorptive capacity is limited



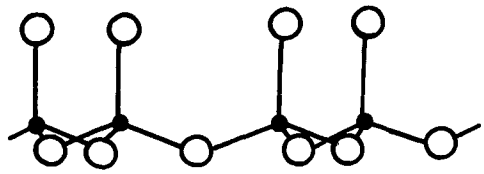
1 (b) Diagramatic edge view of montmorillonite showing two complete layers. The respective crystal units are loosely bound to one another by weak oxygen linkages which allow wide expansion of the lattice. There is high internal adsorptive of water and cations.

1 (c) Illite has the same reneral structural organization as montmorillonite except in respect to the linkages between the cystal unit here atoms supply additional connecting linkages between the crystal units, thus supplementing the oxygen bonding, the expension is shapely lassened by k linkages and adsorptive capacity of the clay lowered

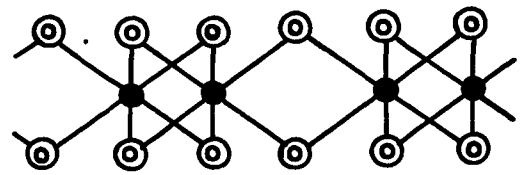
Kaolinite

The name kaolinite for the 'mineral of kaolin' was first suggested by Johnson and Blake[7] in 1867. These are hydrous aluminium silicates of the approximate composition Al_2O_3; $2SiO_2$; $2H_2O$. Their structure first suggested by Pauling[6] was worked out in detail by Gruner[8] and later by Brindley and his colleagues.[9] In kaolinite, a single silica tetrahedral sheet is topped with a slightly distorted gibbsite sheet, both being formed by condensation and splitting off of water between adjoining hydroxyl group in vertex position. All the tips of the silica tetrahedron point in the same direction and towards the centre of the unit made of silica and octahedral sheets. The mineral can thus be described as having a 1 to 1 non-expanding lattice (one layer of silica to one of alumina). Water cannot enter these lattices and this explains the comparatively low moisture content as well as low swelling of these clays. A diagrammatic edge view and some crystal structural features of kaolinite are represented in figures 1 and 2 respectively.

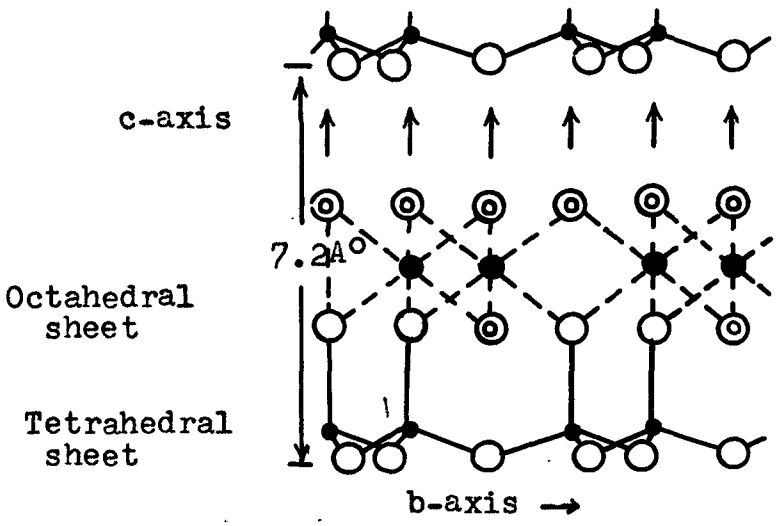
The structural formula may be expressed as $(OH)_8$ Al_4 Si_4 O_{10} (SiO_2 46.54% ; Al_2O_3 39.50%; H_2O 13.96%) and the size of the unit cell as 7.2A°. The general shape of the mineral isolated from the colloidal fraction of the soil is that of a thin, plate like hexagon. Moreover, the space lattice of the mineral is such that there is little substitu-



Tetrahedral silicon sheet

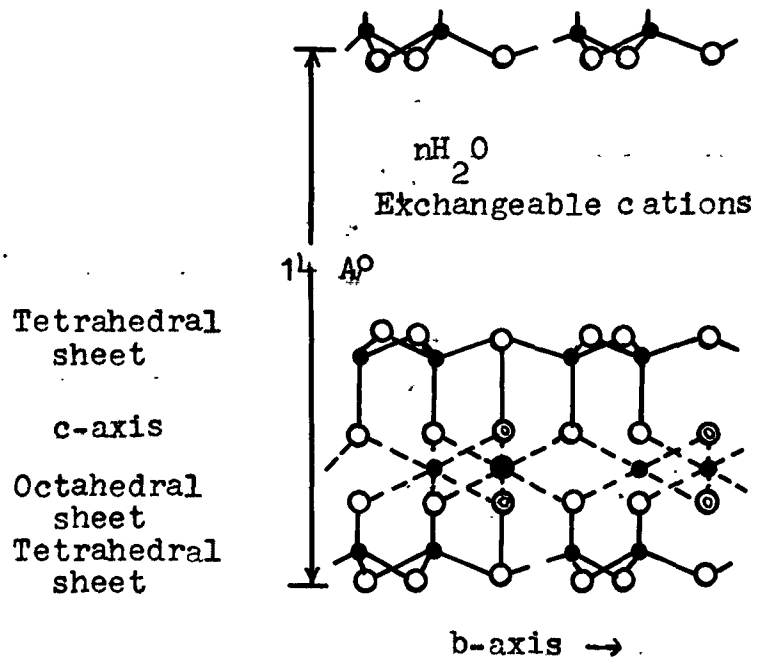


Octahedral gibbsite sheet



Hydrogen bonding	
6 (OH)	- 6
4 Al	+12
4 O + 2(OH)	-10
4 Si	+16
6 O	-12
net charge	0

2 (a) Kaolite, A 1:1 layer silicate mineral



6 O	-12
4(Si,Al)	+16 or less
4O + 2 (OH)	-10
4(Al,Fe,Mg)	+12 or less
4 O + 2 (OH)	-10
4 Si	+16
6 O	-12
net charge	0 or less e.g. -1

2 (b) Montmorillonite, A freely expansible 2:1 layer mineral the inter-layer cations are freely exchangeable.

2 (c) Illite structure is similar to 2 (b) except that the electrical imbalance is set right by the presence of k ions situated between adjacent layers so that the net charge is 0

tion of ions in its structure and there are no unsatisfied valencies on the cleavage surface. Hence there is no adsorption of exchangeable bases on its surfaces under ordinary conditions. Base exchange capacity is thus insignificant except when subjected to very fine grinding.

A projection of the structure of kaolinite on the (100) plane showing the stacking of successive layers in a micro-crystal is shown in figure 3. The structure indicates the position of outer hydroxyls (A) and (B), inner surface hydroxyls (C) and inner hydroxyls (D).

MONTMORILLONITE

The mineral was first studied by LeChatelier[10] and has been assigned the formula $(OH)_4Si_8Al_4O_{20} \cdot nH_2O$. Ross and his colleagues[11] established the identity of montmorillonite as a definite clay mineral species. Now the name, montmorillonite, is used both as a group name for all clay minerals with an expanding lattice (except vermiculite) and also as a specific mineral name. Structurally the mineral consists of three layers, a gibbsite sheet enclosed between two silica sheets with their vertices pointing towards each other and towards the centre of the unit. As in kaolinite, these layers are glued together by primary valence forces due to sharing of oxygen atoms in vertex position. (vide figures 1 and 2).

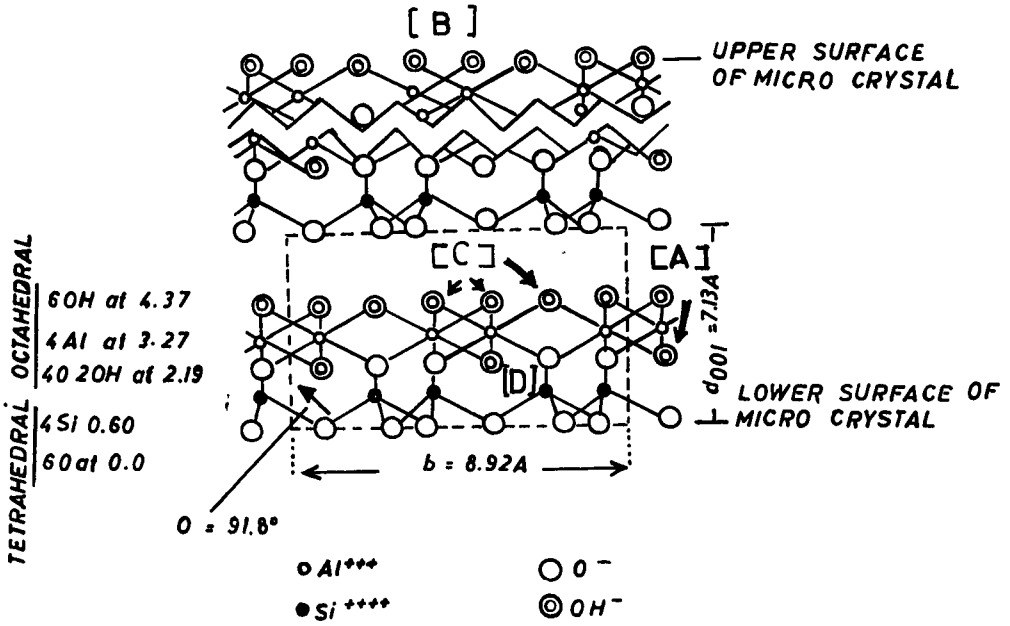


Fig. 3 Projection of the structure of kaolinite on the (100) plane showing the stacking of successive layers in a micro crystal (after Brindley)

[A] [B] indicates "outer hydroxyls"

[C] designates "inner-surface hydroxyls"

[D] indicates "inner-hydroxyls"

X-ray studies have shown stacking of silica-alumina-silica units (in the c direction; layers being continuous in direction a and b) with the result that there exists a weak bond between them and an excellent cleavage. Water and other polar molecules can easily penetrate between the unit layers causing the lattice to expand in the c direction. The c-axis dimension is, therefore, not fixed but varies from 9.6A° to substantially complete separation of the individual layers in some cases. It is for this reason that high volume changes in montmorillonite are induced by moisture variation.

Many familiar names are associated with the investigations on montmorillonite. These are: Hofmann, Endell and Wilm[12], Mac Ewan and Hofmann[13], Marshall[14], Hendricks[15] etc. All of them contributed in ascertaining the physico-chemical behaviour of the mineral vis-a-vis its structure. For example Marshall and Hendricks showed that montmorillonite always differed from its theoretical formula ($(OH)_4Si_8Al_4O_{20}\cdot nH_2O$ - SiO_2 66.7%; Al_2O_3 28.3%; H_2O 5%) because of substitution within the lattice of Al, Mg, Fe, Zn, Cr etc., and of Si by Al or P, giving a series of group minerals. Opinions have, however, differed as to the authencity of the structure proposed by these workers. Edelman and Favejee[16] and McConnell[17] have suggested revisions in these structures in the light of the base exchange capacity data.

Illite

The name illite was proposed by Grim, Bray and Bradley[18] in 1937 for the mica like minerals with a 10Å° c-axis spacing which show substantially no expanding lattice characteristics. The structure of the illite group of minerals follows the pattern suggested by Pauling[6], Mauguin[19], Jackson and Hest[20], Winchell[21] and Hendricks and Jefferson.[22] The basic structure of illite species is very similar to that of montmorillonite with the difference that some of Si^{+4} is replaced by Al^{+3} and the resultant charge deficiency is balanced by K ions between the silica sheets of two successive units. In fact the K ions act as bridges binding the unit layers (gibbsite enclosed between the two silica sheets sharing the vertex oxygen between them) together so that they do not expand in presence of water. (vide figures 1 and 2)

The structural formula of the mineral is given as $(OH)_4K_y(Al_4\ Fe_4\ Mg_4\ Mg_6)\ (Si_{8-y}Al_y)\ O_{20}$. The size of the unit cell is 10Å°. Isomorphous substitution is possible within the lattice resulting in wide variation in composition. Thus, those with very little replacement of silicon approach montmorillonite while those with large replacement approach muscovite. The b.e.c. or these clays is much lower than those of montmorillonite species but higher than those of the kaolinite species.

It has been reported[23] that K ions present in illites can be divided into three categories (i) K ions at surface exchange sites i.e., the outer planar surfaces of the clay minerals, (ii) K ions in interlattice positions near the edges of the clay particles and (iii) K ions in interlattice positions away from the edges. These potassium ions are replaceable from all these positions but the rate and ease of exchange varies, those at the outer planner surfaces being most rapidly replaceable by all cations.

A number of other clay minerals chiefly those of the chlorite group, vermiculite, attapulgite and mixed layer minerals[24] have been reported in soils. The most common of the mixed layer minerals are combination of illite and montmorillonite and of chlorite and vermiculite.

Colloidal Behaviour of Clay Minerals

By virtue of their structure, the clay particles when brought in contact with water pass in to a colloidal state. These suspensions are neither purely lyophilic nor lyophobic. A study of various factors shows that they can be placed as intermediate between the two well defined classes. The ultimate clay particle exists in the form of a very complex anion exposing a highly negative surface. The negative charge arises as a result of isomorphous substitutions[25] of certain electropositive elements like Al^{+3}, Si^{+4} etc., by elements of

lower valence such as Mg^{+2}, Fe^{+3} etc., and also due to ionization of hydroxyl groups attached to silicon at broken tetrahedral places, as in the case of silicic acid.

$$Si\text{-}OH + H_2O = SiO^- + H_3O^+$$

The negative charges created by isomorphous ion substitutions are more uniformly distributed in the plate like clay particles whereas those by ionization at corners and clay edges. Sometimes the soil particles also exhibit a positive surface. The positive charge may originate from exposed octahedral groups which act as bases by accepting protons from the surrounding soil solution.[26]

The negative charge on the clay particle is neutralized by cations which are called exchangeable counter or cogen ions held to the surface by van der waals forces. In the presence of water the compensating cations have a tendency to diffuse away from the layer surface into the bulk solution where they are more or less attracted electrostatically by the charged surface. Thus, an ionic double layer is formed, the clay ion forming the inner ionic layer with a negative surface and the diffused ions forming the outer ionic layer. The structure of the double layer is of great importance for an understanding of the colloidal behaviour of soil systems.[27]

The counter ions which may be Ca^{+2}, Mg^{+2}, H^+, K^+, Al^{+3}, MoO_4^{-2} are easily exchangeable for other cations giving rise to

the phenomenon of ion exchange. The electric double layer on the layer surfaces has a constant charge which is solely determined by the type and degree of isomorphous lattice substitution. Therefore, the unit-layer-surface charge density is independent of the presence of electrolytes in the suspension. Such a double layer is hence unknown to hydrophobic colloids. The double layer in such systems is usually created by the adsorption of potential determining ions; hence the surface potential is constant, and the charge varies with the bulk electrolyte concentration.

There are indications that in many clays specific adsorption forces between the lattice and the counter-ions exist. Hence, a larger than normal fraction of the counter ions will be located on the surface, and a smaller fraction will be in the diffuse layer. Therefore, the Stern-Gouy model would be more commonly applicable to the clay double layer than the Gouy model. An obvious example of specific layer-to-layer water interaction is montmorillonite clay in which potassium ions provide a strong bond between the unit layer surfaces. To what extent cation-to-surface bonding energies play a part in various forms of montmorillonite and other clays is still a matter of controversy.

Apart from the double layer at the flat surface, a possibility of the existence of a positive double layer at the broken edges has been postulated by Van Olphen. His views find support in the work of Hansen on the interaction of

kaolinite suspension with a negatively charged sol. At the edges of the plates, the tetrahedral silica sheets and the octahedral alumina sheets are disrupted and primary bonds are broken. The part of the edge surface at which octahedral sheet is broken may be compared with the surface of an alumina particle and would carry a positive double layer in acid solution with aluminium as potential determining ions and a negative double layer in alkaline media with hydroxyl as potential determining ions. The edge surface of a tetrahedral sheet may be compared with the surface of silica particle. Though silica surface carries a negative double layer its charge is known to become positive in presence of even very small quantities of aluminium ions in suspension owing to the slight solubility of clay, such small concentration of aluminium ions should always be there. Moreover it is possible that silica sheets are always broken at the places where aluminium ions have substituted silicon. Hence a positive double layer would always exist at broken edges.

Ion-exchange

The clay suspensions exhibit the phenomenon of ion exchange. Exchange of both cations and anions is possible by the addition of foreign electrolytes to the suspension. Since the replacement of ions and subsequent filling in by the ions added is dependent on their relative solubility, ionic

adsorption plays the most important role in exchange phenomenon. There are a number of factors on which ionic adsorption is supposed to depend. Those are (i) valency of ion (ii) hydration of ions (iii) ionic radii and (iv) structural configuration of the nucleus of the clay micelle.

The valence and hydration of ions are the most important factors in determining the energy of adsorption and release. Ion exchange will be difficult when the adsorbed ions have got a higher valency or are adsorbed more strongly than those of the lower valency and weakly hydrated ions are more tightly bound up than those containing a large water hull. According to Weigner,[28] for ions of equal valence, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace from the clay surface. Controversy, however, exists as far as the feasibility of the hypothesis on the hydration of ions is concerned. Burner and Fowler[29], Bar and Gonzalez[30], Haven[31] etc., have presented data that do not fit in with cation hydration view point. Recently, Hendricks[32] and his colleagues, after careful investigation studies, have shown that Na^{+}, H^{+} and K^{+} and trivalent ions are not hydrated when adsorbed by clay minerals, while Ca^{++}, Mg^{++} and Li^{+} undergo hydration. According to Bar and Gonzalez the replaceability is related to the polarizability of the ion, increasing polarisation being accompanied by increasing difficulty of exchange. The work of Hofmann and Udell[33] and that of Marshall[34] has indicated that replaceability is also affected by temperature.

Early investigations on various soils had suggested that the replaceability of various cations varied with the nature of adsorption complex. It means that the colloidal clay or to be more precise, the nature of the colloidal clay micelle affects the energy with which a given ion is held. This fact was clearly brought out by Gieseking and Jenny[35], Jenny[36], Dar and Vanderploeg, Schachtschabel[37] and others, who demonstrated that there was no single replaceability series characteristic of all clay minerals.

Another factor, which controls exchange phenomena, is the size of the exchanging ion. It is normally observed that ions of smaller ionic radii are easily replaced by ions of larger ionic radii and vice-versa. Exceptions to this rule are, however, not rare, especially when the size of replacing ion is almost the correct size to fit into the hole in the basal oxygen sheet of the clay minerals[38-39]. The K^+ is the striking example of such a behaviour, because, its ionic radii (2.66A°) is almost the same as the diameter of the oxygen net of oxygen atoms in the silica sheet, and hence it is very difficult to replace.[40]

Many workers[41], including Jenny[42], Ravikovitch[43], Keeney[44], Toth[45] etc., have shown that many soils and clays also exhibit anion exchange reactions. This type of exchange is possible in the following three ways (i) replacement of hydroxyl ions, as shown by the work of Bunzel and Dudenbostel[46] and that of McAuliffe and co-workers[47] on the

basis of infra red spectra and radio isotopic studies respectively (ii) ionic adsorption of phosphate, arsenate, borate etc., on the edges of the silica tetrahedron sheet by virtue of close similarity in the geometry of these anions and the clay mineral structural units as suggested by Hendricks and (iii) exchange reaction through definite spots, which may be considered anion exchange spots and cation exchange spots. According to Schofield[48], such spots do exist, on the basal plane surfaces, due to unbalanced charges within the lattice.

Richhorne work on calcium chabazite showed that ion exchange is a reversible process to which the law of mass action can be applied. As early as 1913 Gans and later Kerr[49] utilized the mass action law in ion exchange studies. The equations derived by Vanselow[50] and Krishnamoorthy and Overstreet[51] have yielded satisfactory equilibrium constants for exchange of metal cations on selected bentonite clay and soil colloids. Gaines has shown that the equations of Vanselow and Krishnamoorthy et.al. are formally equivalent to Donnan equations which have been extensively used in clay studies.

Ion-exchange equilibria are of great practical and theoretical importance and have been studied ever since ion exchangers were recognized as such. Most of the earlier theories were, in essence, descriptions of ion-exchange equilibria by empirical or semiempirical equations. Only in the last fifteen years have consistent theories been developed

which provide essentially correct descriptions of the phenomena and their physical causes.

Ion-exchange equilibrium can be characterized by the ion-exchange isotherms. These isotherms are a graphical representation which, in principle, cover all possible experimental conditions at a given temperature. Equilibrium can also be described in terms of a quantity such as the separation factor, selectivity coefficient, or distribution coefficient. As a rule, these quantities vary with experimental conditions. Thus, any specific value of one of these quantities corresponds to only one point on the isotherm surface.

Ion-exchange isotherms show the ionic composition of the ion exchanger as a function of the experimental conditions. Various ways of representation can be used. As a rule, the equivalent ionic fraction, $\bar{x}_A$, of the counter ion A in the ion exchanger is plotted as a function of the equivalent ionic fraction x_A in the solution, while the other variables are kept constant. The equivalent ionic fraction is defined by

$$x_A \equiv \frac{z_A m_A}{z_A m_A + z_B m_B}$$

or, more generally, by

$$x_A \equiv \frac{z_A m_A}{\sum z_i m_i}$$

where z_A is the electrochemical equivalence of counter ion A,

or D, m is the concentration of counter ion A or B in millimoles per gram solvent or molality, m_i is the concentration of solute i in millimoles per gram solvent or molality and the summation is carried out over all counter-ion species. In a hypothetical system, the ion exchange isotherm may be linear but ion exchangers in general select one counter ion in preference to another. Selectivity thus necessitates a non-linear isotherm.

The preference of the ion exchanger for one of the two counter ions is often expressed by the separation factor. This quantity is particularly convenient for practical applications. The separation factor α_D^A is defined by

$$\alpha_D^A = \frac{\bar{m}_A m_B}{\bar{m}_B m_A} = \frac{\bar{C}_A C_B}{\bar{C}_B C_A} = \frac{\bar{x}_A x_B}{\bar{x}_B x_A}$$

where C_A, $\bar{C}_A$, C_B, $\bar{C}_B$ denote the concentration of solute in moles/litre.

The separation factor is the quotient of the concentration ratios of the two counter ions in the ion exchanger and the solution. If the ion A is preferred, the factor α_D^A is larger than unity, and if B is preferred, the factor is smaller than unity. The numerical value of the separation factor is not affected by the choice of the concentration units.

The separation factor is usually not constant, but depends on the total concentration of the solution, the temperature, and the equivalent fraction x_A.

Sometimes instead of the separation factor, the selectivity coefficient can be used for describing ion-exchange equilibria. The molal selectivity coefficient is defined by

$$K_B^A = \frac{\bar{m}_A^{|z_B|} \; m_B^{|z_A|}}{\bar{m}_B^{|z_A|} \; m_A^{|z_B|}}$$

Molarities or equivalent ionic fractions can be used instead of molalities when we get the molar and rational selectivity coefficients, respectively.

For counter ions of equal valence ($z_A = z_B$), the numerical value of the molal, the molar, and the rational selectivity coefficients are identical and are related to the separation factor by

$$K_B^A = K'^A_B = {}^N K_B^A = (\alpha_B^A)^{|z_A|} \quad (z_A = z_B)$$

where K'^A_B and ${}^N K_B^A$ are the molar and rational selectivity coefficients, respectively. For counter ions of different valences, the numerical value of the selectivity coefficient depends on the choice of the concentration scale. The

general relation is

$$\left(\alpha_B^A\right)^{|z_A|} = K_B^A \left(\frac{\bar{m}_A}{m_A}\right)^{|z_A| - |z_B|} = K'^A_B \left(\frac{C_A}{C_A}\right)^{|z_A| - |z_B|}$$

$$= {}^{J}K_B^A \left(\frac{\bar{x}_A}{x_A}\right)^{|z_A| - |z_B|}$$

The essential difference between separation factor and the selectivity coefficient is that the latter contains the ionic valences as exponents. Thus, the separation factor is usually quite different from the selectivity coefficient, if the valences of the competing counter ions are not equal. In such cases, the selectivity coefficient remains more nearly constant when the experimental conditions, particularly, the total solution concentration, are varied.

In certain practical applications, equilibrium is most conveniently expressed in terms of the distribution coefficients of the counter ions, the molal and molar distribution coefficients are defined by

$$\lambda_i = \frac{\bar{m}_i}{m_i} = \frac{x_i}{\bar{x}_i}\,\frac{\bar{m}}{m}$$

$$\lambda'_i = \frac{\bar{C}_i}{C_i} = \frac{\bar{x}_i}{x_i}\,\frac{\bar{C}_i}{C}$$

where λi is molal distribution coefficient and $\lambda' i$ is molar distribution coefficient respectively or in other words the distribution coefficient is defined as the number of milliequivalents of an ion adsorbed per gram of exchanger divided by the number of milliequivalents of that ion per ml remaining in solution at equilibrium, and is, therefore, a direct measure of the extent to which an ion is removed from solution when the exchanger is added. The coefficients increase with dilution of the solution. For any given condition, the distribution coefficient can be calculated from the selectivity coefficient.

In theoretical studies, the thermodynamic equilibrium constant is occasionally used. This quantity is defined by the thermodynamic relation

$$\Delta G^{\circ} = - RT \ln K_D^A$$

where ΔG° is the standard free-energy change of the ion exchange and the sorption and desorption of solvent and electrolytes by which this process is necessarily accompanied, and where K_D^A is the equilibrium constant. In contrast to the separation factor, the selectivity coefficient, and the distribution coefficient, which all refer to a given set of experimental conditions and thus correspond to one specific point on the isotherm surface, the equilibrium constant is an integral quantity characteristic of the whole isotherm surface and is a true constant depending on temperature only.

Accordingly, the equilibrium constant gives no information about the exact counter-ion distribution under any particular experimental conditions.

The relation between equilibrium constant and activities of the counter ions in the ion-exchanger and the solution depends inherently on the definition of the activities and, hence, on the model on which the treatment is based. A simple relation exists only if electrolyte sorption and changes in swelling can be neglected. In this case the equilibrium constant is

$$K_B^A = \frac{\bar{a}_A^{|z_B|} \; a_B^{|z_A|}}{\bar{a}_B^{|z_A|} \; a_B^{|z_B|}}$$

The nature of the equilibrium constant obtained depends on the choice of the standard and reference states and thus it can be molal or rational equilibrium constant.

<u>Acid Clays and their Base Exchange Reactions</u>

When clays are subjected to acid leaching, or are electrodialyzed, or passed through a column of ion exchange resins, hydrogen ions are preferentially adsorbed by clay particles resulting in the formation of acid clays. A clay crystal presents two kinds of surfaces, planar and lateral

to a contact solution, and the acid character of clay is an attribute of those surfaces. The question whether H^+ or Al^{3+} are the exchangeable cations in clay acid is still open. Different ideas have been put forward to account for the acidic character of clays. According to Marshall[52], Hendricks[53], Kelly and Nagelschmidt[54], isomorphous replacements in the clay lattice give rise to acidity in clays. Millikan, Mills and Ohland[55], however, do not think that such replacements are the true cause of the acid character of clays. According to them clay acids is not an Arrhenius acid having ionisable H^+ (and or Al^{3+}) ions. On the other hand, it is more like a Lewis acid in which on the addition of a base to an acid clay, a shift in coordination number of aluminium on the surface takes place from six to four as follows

$$S_6 + OH^- \rightleftharpoons S_4^- + H_2O$$

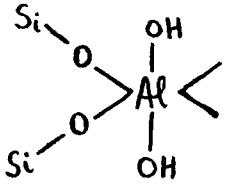
where S_6 represents neutral aluminium, and S_4, aluminium in four coordination state. The cation of the added base is held up at the S_4 site as follows

$$S_4^- + Na^+ \rightleftharpoons S_4^- .. Na^+$$

The above mechanism does not account for the now established fact that H^+ ions, as well as, Al^{3+} ions are liberated from acid clays by treatment with neutral salts[56,57,58]. To explain this behaviour, supporters of the above Mg0 mechanism have suggested other possible acidic principles which by dissociation could give rise to H^+ or Al^{3+} ions. According

to Coates[59] et al. the Arrhenius acid character functions below pH-7, and the Lewis acid behaviour is evident at higher pH values.

Hydroxyl groups[60] are present in clay crystals as structural constituents. They may also occur at the lateral surfaces resulting from a hydrolysis of broken Si-O-Si bonds and in case of montmorillonite[61] such groups are present in the silica layer as structural constituents. According to Jackson[62] the aluminium ion bonds through oxygen form a variety of functional groups which provide the cation exchange site of soil layer silicate clays. The bonding is central to soil acidity through not only the acidic aluminohexahydronium monomeric cations but also through the weakly acid Al- OH_2... OH pair at edges of polymerised hydroxy aluminium structures in silicate clays. These cation exchange site play an important role in determining the nature of soil acidity. Caldwell and Marshall[63] and also Mitra and Mathur[64] attribute a part of the acid character of attapulgite to groups such as



Mitra and Rajagopalan think that OH groups are solely responsible for the acid character of kaolinite. They also obtained titrimetric evidence which led to show that two-third of the base combining capacity of hydrogen mica was due to its exposed

structural OH group and the remaining one-third was traceable to the negative isomorphous charge of the surface.

The results on the titrations of clay suspensions with bases reveal that the pH variations are in a manner comparable to those of weak acids.[66,67,68]. The interaction between the colloidal clay acids and alkalis necessitates the postulation of mobile and bound hydrogen ions which constitute the electrical double layer. The inflections obtained during the titrations of clay acids are explained on the concepts of crystallinity and the layer lattice structure which postulates the existence of exchange spots with different bonding energies.[69]

Both conductometric and potentiometric titrations with H-clays may be employed for characterising clay minerals. The latter have been more usefully employed in characterising the soil acids. Starting with the pioneering investigations of Bradfield, one comes across the names of Baver and Scarseth[70], Denison[71], Mattson[72] and others, who in their own way contributed towards the interpretation of the titration curves and the nature of soil acidity.

Chakraverti[73] and more recently Sarkar and Chatterjee[74], while working with mixtures of pure clay minerals, have noticed that in such cases, the inflection point due to individual minerals, often merge with each other, so that all the inflection points are not separately available in the mixture and from potentiometric titrations alone, it may not be possible

to get a clue about the identity of the minerals in a soil. Moreover, the inflections given by the clay acids are not sharp. To overcome such a defect, titrations in non-aqueous media can be suggested. The idea for non-aqueous titrations was first suggested in the work of Folin and co-workers[75] some fifty years ago. A number of organic solvents have been suggested by various workers[76] for non-aqueous titrations of weak acids.

INTERACTION OF CLAYS AND ORGANIC COMPOUNDS

Studies on clays have revealed that they extensively form complex compounds with many organic substances. An excellent survey of adsorption of organic material by clay minerals and of clay organic reactions has been given by Mac-Ewan[77] and Grim.[78] Much of the work on clay organic complexes pertains to reactions between montmorillonite, halloysite and vermiculite. Hendricks[79] and Grim et. al.[80] found that small organic molecules replace the exchangeable cations on montmorillonite quantitatively, but with larger molecules, the exchange is incomplete due to the 'cover up effect'. The ions are held by van der Waals forces and strong electrostatic bonds at the sites of charge.

Organic anions are adsorbed at the edges of the clay particles. Organic cations, on the contrary, are adsorbed on the negative face surfaces of the clay. This is evident

from the much larger adsorption capacity of the clay for the cations and also from the increase of the basal spacing of montmorillonite clays after treatment with organic cations. Thus, when an amine salt, such as $R\text{-}NH_3^+Cl$, or a quaternary ammonium salt or base ($R_4N^+Cl^-$ or $R_4N^+OH^-$) is added to clay water suspension, the organic cations replace the cations which were originally present on the clay surfaces; in other words, 'exchange adsorption' takes place. There appears to be a strong preference of the clay for the organic cations, which are often practically quantitatively adsorbed until all the exchange positions are occupied by the organic cations. The amino groups become strongly attached to the clay surface.

The adsorption of organic cations is sometimes not limited to an amount equivalent to the cation exchange capacity of the clay, e.g., for a quaternary ammonium compound with a long chain and a montmorillonite clay, adsorption of about $2\frac{1}{2}$ times the cation exchange capacity of the clay has been observed. The excess of the organic salt is physically adsorbed by van der Waals linking of the hydrocarbon chains of the exchange adsorbed cation and there on the excess organic molecules. The ionized groups of the physically adsorbed molecule will point towards the water phase.

Many organic compounds with a dipole character are adsorbed on the layer surfaces and probably also on the edge surfaces of the clay, in analogy with the behaviour of water. The adsorption energy of many of these compounds is probably

of a magnitude comparable with that of water; they can displace adsorbed water from clay. But frequently the organic compounds can be removed from the clay by washing with water. As in case of adsorption of water on clays we do not know exactly to what extent the polar groups of the organic molecules associate with the counter ions of the clay and to what extent they are hydrogen bonded with the oxygen surface.

Several reactions between dry clays and organic compounds occur, or are inferred to occur, which would indicate that, for example, in an acid bentonite clay, OH groups exist on the surface.[81] These OH groups would be bound to silicon, as in a silanol, the silicon analogon of alcohols. Such silanol groupings have been found to exist in montmorillonite.[82] However, the formation of clay organic reaction products in which the organic compounds are chemically bonded with the surface has been doubted. It has been pointed out for example that residual adsorbed water on the clay might have caused hydrolysis of the organic reactants, the resultant products of hydrolysis being physically adsorbed by the clay. There is still evidence for the interlayer penetration of organic compounds in some clays like kaolinite.[84]

According to Mendricks[85] the organic ions are held to the clay surface by van der Waals forces in addition to coulombic forces. Larger ions are held more strongly because of greater van der Waals forces. The coulombic forces are further supplemented by C-H ... O bonds between the organic molecules and clay mineral surfaces.

Adsorption

Interesting studies have been made on the mechanism of adsorption of organic compounds on siliceous and aluminous surfaces.[86-90] It has been observed that several factors such as lattice configuration of the adsorbent, its exchangeable cations and their hydration, the heat treatment of the adsorbent, atomic and molecular structure of the adsorbate, its solubility and concentration in the solvent and the solvent itself, the orientation of the molecules and the environmental conditions affect adsorption.

Chemically soils are alumino-silicate and as such characterized by possessing exposed surface layers rich in oxygen atoms and the hydroxyl groups. These surfaces are basically highly polar in character and possess an intense residual force. Generally these forces are responsible for holding the other ions or molecules at the surface temporarily or permanently depending on the nature of the forces operating at it. Residual valence forces, dipolar attractions or any other physical forces of the Van der waals type lead to adsorption whereby the molecules are held temporarily, whereas chemical or electrostatic forces give rise to permanent building and molecules stay permanently on the surface. Bradley and Grim[91] believed that the coulombic forces were further supplemented by C-H .... O bonds between organic molecules and clay mineral surfaces and that the organic

molecules arranged themselves in parallel layers between the structural sheets of clay mineral and lied as flat as possible.

Studies on viscosimetric[92] constants of suspensions of clay-polymer complexes have revealed that H-montmorillonite polymer complexes consisted of an edge to edge linkage of clay particles through lattice-aluminium-carboxyl bonds whereas aluminium montmorillonite permitted three kinds of linkage: edge to edge (as with H-montmorillonite), external flat surface to surface (producing a stacked structure) and surface-to-edge, the last two involving exchangeable aluminium carboxyl bonds.

Barrer and Rowy and Barrer and MacLeod[93] have shown that in montmorillonite saturated with certain short chain amino and quaternary ammonium compounds, the amino cations were largely present as an incomplete monolayer between the unit layers of the montmorillonite and that the individual cations act as pillars in preventing collapse of the montmorillonite lattice on drying. They have also demonstrated that the space between the cation pillars is available for the sorption of both polar and non-polar groups.

Farmer and Mortland[94] in an infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite have proposed that pyridine has a tilted configuration in sodium montmorillonite than

a normal or perpendicular plane as proposed by Greenwood[95] is that a surface pyridine molecule is hydrogen bonded to a surface hydroxyl group and can account for the conversion of polarised molecules into pyridinium ions. The shift to higher frequencies appears to exclude the suggested C-H .... O hydrogen bonding.

Studies on the mechanism of adsorption of ammonia by several workers[96-99] reveal that the adsorption of ammonia by clay surfaces principally involves association with a proton, the proton coming from several sources. Jacobs and Hallard[100] believe the adsorption to be similar to that which occurs in the formation of inorganic salts, namely the mutual attraction between unshared electrons in the NH_3 molecules and ionic centres of positive charge. A reduced rotation of NH_3 by the H of Al cystals is ascribed to the possibility of exchangeable H and Al on kaolinite surfaces occurring as hydroxy complexes. A significant amount of NH_3 could be adsorbed to the weak acid hydroxyl groups on the broken clay edges.

In case of some extract montmorillonite, a reaction in the basic pyridine and the surface was indicated by Mehlich and Hendricks[101] for the adsorption of pyridine. Further, a considerable part had initially adsorbed pyridine at the water vapour pressure. Physically adsorbed pyridine can be removed by washing with water vapour but chemisorbed pyridine is not removed.

Infrared spectrometry[102] on clays show that there are three type of surface OH groups in clays viz., those at the edges, those at outer and inner surfaces as well as the inner hydroxyls. The development of acidity in NH_4-montmorillonite is explained as being due to thermal decomposition of NH_4^+ with loss of NH_3 and liberation of proton and that in Mg- and Li-montmorillonite as due to proton liberation by reaction between residual water molecules and lattice OH groups. The monovalent and divalent cations of the clay are found to participate water in the outer and inner spheres of coordination. Polar molecules such as those of pyridine and nitrobenzene could replace water from the outer spheres of coordination forming hydrogen bonds. Ammonia and ethylamine are found to form tetra-coordination complexes with ions like Cu^{++} displacing water entirely.

Besides the adsorption of the organic molecules on the clay minerals, there is another aspect worth considering. It concerns with the adsorption of the organic compounds by clay mineral aggregates. Very few papers exist on this aspect are available in literature. Recent studies by Brindley and Cowan,[103-104] Bodden and Smith[105] have shown that water acts in competition with organic matter for sites on the clay surface. In such cases, the pH of the suspension also influences the adsorption characteristics of clays.

Bodden and Young[106] on the basis of their studies on

the adsorption of quinoline by clay suspensions have shown that the adsorption of the organic molecule depends on its concentration, pH, salinity and temperature and that both exchange and molecular adsorption are operative. Mackenzie[107] has shown that montmorillonite adsorbs many organic compounds like monohydric and dihydric alcohols, nitriles etc., but when the clay was immersed in a dilute aqueous solution of these compounds, preferential adsorption of solvent occurs.

The present knowledge of clay-organic-complexes is thus rather sketchy, and is mostly empirical. We have a general and reasonable idea about orientation, packing and apparent van der Waals dimensions in the organic layers but much still has to be learned about the bonding mechanism and the energetics of adsorption. A further quantitative study of these complexes may prove to be specially fruitful for the understanding of the interaction of surfaces on organic molecules in heterogeneous media; because much more information can be obtained on the molecular arrangement of the adsorbate in complexes, than on single surfaces. Moreover, the ratio of the amount adsorbed to amount of adsorbent is very favourable in these complexes. Effects of the strong local electric field on resonance in aromatic molecules will be of particular interest.

Adsorption Isotherms

Inspite of its technological importance fundamental

investigations on adsorption especially at the liquid-solid interface proceeded only slowly. The Freundlich equation was applied indiscriminately to all isotherms limited to adsorption from dilute solutions. It took many years for concentrated solution to be explored and for the results of the explorations to be widely appreciated. The Freundlich isotherm was found to describe the behaviour of adsorption only approximately. Thus, isotherms for adsorption on charcoal when plotted for the whole range of concentration could not be fitted into the Freundlich equation nor in any modification of it. A model for the chemisorption process was presented by Langmuir in 1916. According to him, in the case of chemisorption the adsorbed layer was unimolecular in thickness and there existed a dynamic equilibrium between the adsorbed and unadsorbed gas molecules. From thermodynamic considerations Gibbs derived an important relation between the adsorption in the surface layer binding the two phases and the rate of change of surface tension of the surface with change in concentration of the solute. None of these concepts, however, could explain the results of adsorption in different cases. It was tacitly assumed that the second component was not involved in the adsorption process and could be regarded merely as a space in which the solute has play. This concept is now no longer tenable. Preferential or selective adsorption of the second component is found possible and an equation

for a composite isotherm is proposed as follows

$$\frac{n_o \Delta x}{m} = n_1^s (1-x) - n_2^s x$$

This equation is found applicable to adsorption from all solutions, of whatever concentrations and can also account for multilayer adsorption.[108] Thus, in a few cases it is found that although the composite isotherm had a linear section yet the adsorption is two molecules thick.[109] During chemisorption process it is normally supposed that preferential physical adsorption of one component occurs on the top of the first layer. To account for such cases the above equation is modified to give

$$\frac{n_o \Delta x}{m} = (n_1^s)_{chem} + (n_1^s)_{phys} (1-x) - n_2^s x$$

In general, composite isotherms show a smooth variation with composition of solution. In some cases, however, steps and sharp discontinuities are observed. These are attributed to the appearance of a second layer of adsorbate on the top of the first[110] or due to a phase change in the adsorbate. Sharp breaks in the isotherms can also be due to the change in the orientation of the adsorbate. Venturello and published a series of papers in which he has

presented such isotherms for adsorption by inorganic solid, alumina, silica gel, magnesium hydroxide and calcium carbonate from solutions of dye stuffs in water and of iodine in organic solvents.[111-112] It is suggested that different parts of the isotherm correspond to adsorption on sites of differing energy due to hetrogeneity in the surface.

A classification of the diferent isotherms obtained during adsorption was proposed by Giles.[113] The Langmuir type curve was obtained when there was no strong competition from the solvent for sites on the surface and the adsorbate had linear or planner molecules. A S shaped curve was obtained if the solvent was strongly adsorbed, there being a strong intermolecular attraction within the adsorbed layer and the adsorbate was monofunctional. An H shape occurred when there was high affinity between the adsorbate and adsorbent as in very dilute solutions during chemisorption or during adsorption of polymers or ionic micelles. A C type of curve was obtained when there was constant partition of the adsorbate between the solution and the adsorbent as in textile fibres.

A number of isotherms show steps as has been discussed above. In general the steps appear to mark a phase change in the adsorbed layer or the onset of the formation of a second molecular layer after completion of the first. A less common shape involved is a wave. The change in slope occurs at a small value of adsorption and can indicate a form

of cooperative[114] adsorption, which indicates some degree of deformation in packing in the crystalline state.

Plateaus and maximas have been observed in adsorption isotherms. A long plateau in the adsorption isotherm is indicative of the fact that a high energy barrier has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the first degree. The solute has high affinity for the solvent, but low affinity for the layer of solute molecules already adsorbed. It is perhaps significant that adsorptions of ionic micelles give curves with long plateau; in these cases the surface of the solid, when covered, will tend to repel other micelles holding the same charge.

A short plateau must mean that the adsorbed solute molecules expose a surface which has nearly the same affinity for more solute as the original surface had. Second rise and second plateau are attributed to the development of a fresh surface on which adsorption can occur, the second plateau representing the complete saturation of the new surface, though this stage is not always realisable. Occasionally a fall in slope occurs after the first inflection. This is probably due to association of the solute in solution i.e. with increase in concentration the solute-solute attraction begins to increase more rapidly than the substrate-solute attraction.

X-RAYS AND CLAY MINERALS

In 1912 Laue and his associates noticed that crystals can act as diffraction gratings to X-rays. Immediately following this discovery Debye and Scherrer in Germany and Hull in the United States discovered that there existed a characteristic X-ray diffraction effect for a fine grained crystalline aggregate. Further research on single crystals was responsible for revealing the arrangements of atoms in the crystal itself. A knowledge of the way in which atoms are geometrically arranged in crystals brought about a revolution in modern science, particularly in Chemistry and Solid State Physics. X-ray studies have played a vital role in clay mineral researches as reported by Brindley,[115] Bragg,[116] Buerger,[117] James[118] Wilson[119] and others.[120]

Differential Thermal Analysis

Thermal analysis, although used to supplement the results obtained by other methods of clay mineral identification, lives a considerable amount of information on clay mineralogical investigations. The method originally due to Le Chatelier[121] and applied to soils by Agafonoff and Journavsky[122] is based on the recording of endothermic and exothermic changes during the heating of clay minerals. By measuring the size of the peaks and troughs on the heating

curve, a quantitative estimate of the amount of a given material may be obtained.[123] Excellent reviews on the subject have been published and a valuable account of the Russian developments is afforded by the 1953 Congress report edited by Borg.[124] The DTA studies have also proved useful in elucidating the nature of clay organic interactions.

TRACE ELEMENT STUDIES

A study of trace elements in relation to soils has gained considerable importance during the last two decades. These elements have been found to play an important role in the life processes of plants and animals and their deficiencies and toxicities have considerably affected crop production and animal diseases.[125] Besides neutralising harmful conditions in soils, copper plays an important role as nutrient in oxidation reduction enzyme[126] and together with cobalt its deficiency may cause several forms of diseases to cattle fed on crops grown on such soils. The growth of leguminous crops is found to be retarded by molybdenum and water soluble boron[127] whose deficiencies result in deformities in cauliflower, tomatoes and lettuce. These elements also affect nitrate utilisation and calcium uptake by the roots. Iron and manganese[128] are the most abundant of the trace elements but under alkaline and calcareous conditions

they mostly remain inactive and unavailable for plant nutrition. Only ferrous iron from among total iron is considered to be active and available to plants. Besides their function as nutrients, the trace elements play an important biological role and an excess or deficiency leads to crop failure and diseases like chlorosis in the fruit trees. According to Goldschmidt alluvial soils derived from sandstones, shales etc., may show deficiency of zinc, copper, cobalt and iron.

CORRELATION AND COEFFICIENTS

In most of the above studies, the value of correlation coefficients ~~are~~ have been, generally, calculated from the product moment correlation coefficient formula viz:

$$r = \frac{Cov\ (x,y)}{\sqrt{V(x)\ .\ V(y)}}$$

where x and y are the two variables i.e., the quantities between which the correlation coefficient are to be calculated. The above formula can be more simply written as:

$$r = \frac{\sum x.y - \frac{\sum x.\ \sum y}{n}}{\sqrt{\left(\sum x^2 - \frac{(\sum x)^2}{n}\right)\ \left(\sum y^2 - \frac{(\sum y)^2}{n}\right)}}$$

where n is the number of samples analysed and $\sum$ represented

summation of readings.

In the present studies the above simplified expression is utilised for the calculation of correlation coefficients between the physico-chemical properties of the soils and the trace element status on adsorption. The significance of r is tested by setting statistics under the null hypothesis, Ho, $\rho = 0$

$$|t| = \left| \frac{r \quad n-2}{\sqrt{1 - r^2}} \right| \sim t_{n-2}$$

at a 5% level of significance.

When the calculated value of 't' is found to be greater than the tabulated value of 't' at 5% level of significance and for 30 or 15 degree of freedom, Ho is rejected indicating a significant value of r, which means a significant correlation between the values under consideration.

When the calculated value of 't' is less than the tabulated value, Ho is accepted indicating that there is no significant correlation between the quantities under consideration (Tabulated value of t at 5% l.s. = 2.042)

Influence of the Investigations

The phenomenon of adsorption of organic compounds

Studies on trace metals are all the more important in view of Aligarh having been selected as the only district in U.P. State for Intensive Agricultural Development Programme and on account of its large alkaline, saline and barren areas of usar soils which need improvement.

THE PROBLEM

The investigations described in this thesis have been carried out from two angles. The first part of the thesis deals with studies on the distribution of trace elements in Aligarh soils. Such studies have been carried out extensively in the part on some soils of India and the world and have a great practical and theoretical value in the improvement of soils. However, here the approach is towards 32 samples collected from the typical soil profiles of Aligarh district, studies on which have not been reported so far. Using statistical methods of analysis correlations coefficients have been developed between the physico-chemical properties of the soils and the trace elements.

The second part of the thesis describes the results of some fundamental investigations carried out on the interactions of standard clays with nicotine. Under this part are included colorimetric investigations, and sorption and desorption processes, as well as X-ray and thermal investiga-

tions on clay-organic interactions. The chief objective of these physico-chemical investigations on the interactions of nicotine with the two most important series of homoionic acid and base saturated clays viz., montmorillonite and illite was to obtain information on the stoichiometry of the reactions under differing conditions of pH and hence to obtain a more clear understanding of the mechanism of adsorption, and the specificity of the different reactive sites in montmorillonite and illitic clays. Adsorption studies on standard clays have often been made and the nature of clay organic bond investigated but the information available on adsorption mechanism particularly in the area of edge-surface chemistry is still inadequate and needs investigation. Also included under this part is a fundamental investigation of the thermodynamics of cobalt (II) - sodium exchange on montmorillonite. The thermodynamic formulation of this exchange-equilibria, though not very useful from the point of view of seeking information on the physical causes of the behaviour of the system and on the mechanism and forces of adsorption has, however, the advantage of being thermodynamically exact.

The subject matter of the thesis entitled "Physico-chemical and Trace-element studies on Clays and Soils" has been divided, for the sake of convenience, in the following groups:

(i) Profile distribution of trace elements in some typical

soils of Aligarh district.

(ii) Physico-chemical studies on the interaction of nicotine with montmorillonites.

(iii) Physico-chemical studies on the interaction of nicotine with illites.

(iv) Thermodynamics of Na-cobalt (II) exchange on montmorillonite.

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Chapter II

[illegible]

PROFILE DISTRIBUTION OF [illegible] IN SOME TYPICAL SOILS OF ARIZONA AND NEW MEXICO

Of the sixteen elements known to be essential for plant and microorganism growth, seven are required in such small quantities that they are called micronutrients or trace elements. These are iron, manganese, zinc, copper boron, molybdenum and chlorine. Other elements such as silicon, vanadium and sodium appear to be helpful for the growth of certain species. Still others such as cobalt, iodine and flourine have been shown to be essential for animal growth, but apparently not required by the plants.

Micronutrients have become of more wide-spread concern during the past fifteen years than was the case earlier. One common characteristic of all the micronutrients is that they are required in very small amounts. Also, they are all harmful when the available forms are present in the soil in large quantities. Molybdenum, for example, may be beneficial if added at rates as little as $\frac{1}{2}$ to 1 ounce per acre, while 3 or 4 ounces of available molybdenum per acre may be toxic to most plants.

As might be expected, the specific role of the various micronutrients in plant and microbial growth process is not well understood.[1,2] The meagre information available,

however, suggests that several trace elements are effective through certain enzyme systems. For example copper, iron and molybdenum are capable of acting as "electron carriers" in enzyme systems[3] which bring about oxidation reduction reactions in plants. Apparently such reactions, essential to plant development and production, will not take place in the absence of these micronutrients. Zinc and manganese also function in enzyme systems which are necessary for important reactions in plant metabolism.

Molybdenum and manganese have been found to be essential for certain nitrogen transformations in microorganism as well as in plants. Molybdenum is thought to be essential for the process of nitrogen fixation, both symbiotic and nonsymbiotic. It must be present in plants if nitrates are to be metabolized into amino acids and proteins. In each case molybdenum apparently is an essential part of the respective enzyme system which facilitates the nitrogen change.

Zinc is thought to be concerned in the formation of some growth hormones and in the reproduction process of certain plants. Copper is involved in respiration and in the utilization of iron. A boron[4] deficiency decreases the rate of water absorption and of translocation of sugars in plants and iron is essential for the synthesis of proteins contained in the chloroplasts.

Parent materials tend to influence, in a practical way, the micronutrient contents of soils, perhaps even more so than that of macronutrients.[5] Deficiencies of trace elements can frequently be related to low contents of the micronutrients in the parent rocks or transported parent material. Similarly, toxic quantities are commonly related to abnormally large amounts in soil forming rocks and minerals.

As might be expected, the scant data available indicate that sources of the seven micronutrients vary markedly from area to area. Also because of the extremely small quantities of some of these elements present in soils and in rocks, little is known about the specific compounds in which they are found. All of the micronutrients have been found in varying quantities in igneous rocks. Two of them, iron and manganese, have prominent structural positions in certain of the original silicate minerals. Others may also occupy structural positions as minor replacements for the major constituents of silicate minerals. As mineral decomposition and soil formation occur, the mineral forms of the micronutrients are changed, just as was the case of macronutrients. Oxides, and, in some cases, sulphids of elements such as iron, manganese and zinc are formed. Secondary silicates, including the clay minerals, may contain considerable quantities of iron and manganese. The micronutrient cations that are released as weathering occurs are subject to colloidal

absorption just as are the Ca or H ions. Actions such as the borate and molybdate may suffer absorption of reaction in soils similar to that of the phosphates. Chlorine, which is by far the most soluble of the group, is added to the soils in considerable quantities each year through rain water. Its incidental addition in fertilizers and in other ways helps prevent the deficiency of chlorine under field conditions.

Organic matter is an important secondary source of some of the trace elements. In uncultivated profiles there is a greater concentration of micronutrients in the surface soil, much of it presumably in the organic fraction. Although the elements thus held are not always readily available to plants, their release through decomposition is undoubtedly an important fertility factor.

Micronutrients are most apt to limit crop growth[6] under the following conditions: (1) highly leached acid sandy soil; (2) muck soils; (3) soils very high in pH; and (4) soils which have been intensively cropped and heavily fertilized with macronutrients only.

The micronutrient contents of organic soils are dependent upon the extent of the washing or leaching of these elements into the bog area as the deposits formed. Intensive cropping of muck soils also accentuates trace element deficiencies. Eventually the micro, as well as,

macronutrients must be supplied in the form of fertilizers if good crop yields are to be maintained.

The soil pH and calcium content[7] have a marked influence on the availability of all the micronutrients except chlorine. Under very acid conditions, molybdenum is rendered unavailable, while at high pH values all the cations are unfavourable affected. Overliming can bring about the deficiency of iron, manganese, zinc, copper and even boron. Such conditions occur in nature in many of the calcareous soils.

Each of the four micronutrient cations (Fe, Mn, Zn and Cu) are influenced in a characteristic way by their soil environment.[8] However, certain soil factors tend to have the same general effects on the availability of all of them.

As the pH is increased, the ionic forms of the micronutrient cations are exchanged to the hydroxides. All the hydroxides of the trace element cations are insoluble, some more so than others. The exact pH at which precipitation occurs varies from element to element and even between oxidation states of a given element. In any case, however, the principle is the same- at low pH values the solubility of micronutrient cations is at a maximum and as the pH is raised, their solubility and availability to plants decrease. The desirability of maintaining an intermediate soil pH is obvious.

Three of the trace element cations are found in soils in more than one valence state. These are iron, manganese and copper. The lower-valence states are encouraged by conditions of low oxygen supply and relatively higher moisture level. The changes from one valence state to another are in most cases brought about by microorganisms and organic matter. In some cases the organisms may obtain their energy directly from the inorganic reactions. The oxidized state of iron, manganese and copper are generally much less soluble at pH values common soils than are the reduced state. For example, the hydroxide of trivalent ferric iron precipitates at pH values near 3.0 while ferrous hydroxide does not precipitate until a pH of 6 or higher is reached.

Lime induced chlorosis (iron deficiency) in fruit trees has been found to be encouraged by the presence of the bicarbonate ions. The chlorosis apparently results from iron deficiency on soils with high pH. In some way the bicarbonate ion interferes with iron metabolism. Zinc, manganese and iron ions are found as integral elements in certain silicate clays, especially of the 2 to 1 type. Depending on conditions those ions may be released from the clays or they may be fixed by them. Since the total quantities of iron and manganese in a soil is sufficiently large, the fixation of these elements is somewhat more

serious, however, since the total amount of this element in soils is usually quite small.

Each of the four micronutrient cations may be held in organic combination. Microorganisms also assimilate them as they are apparently required for many microbial transformations. The organic compounds in which these trace elements occur undoubtedly vary considerably, but they include proteins, amino acids and constituents of humus and other acids such as citric and tartaric. Among the most important, are the so called organic complexes which are a combination of metallic cations and certain organic groups. These complexes may protect the micronutrients from certain harmful reactions, such as precipitation of iron by phosphates and vice versa. On the other hand, complex formation may reduce micronutrients availability below that necessary for normal plant needs.

On soils high in organic matter, complex formation by copper is thought to be responsible for the deficiency of this element. Regular applications of copper-containing salts may be necessary for the normal production of vegetables on these high-organic-containing soils. Zinc deficiencies have also been attributed to reactions with organic matter. Advantage has been taken of the complex-forming tendencies of manganese, copper, zinc and especially iron in the development of synthetic compounds called chelates.[9]

These compounds can be used to supply selected micronutrients in forms which protect the cations from some harmful inorganic reactions in soils and at the same time the chelated nutrients can be utilized by growing plants.

The work described in the present chapter deals with the trace element status of the typical soils of Aligarh district. Samples from the whole soil profile in each typical case have been examined in order to obtain precise information on the trace element distribution in the various horizons.

GENERAL DESCRIPTION OF THE ALIGARH SOILS

The studies described in this chapter deal with the trace element status of the soils of Aligarh district. A brief resume of the district and its soils is given hereunder:

Aligarh covers an important area among the district of Uttar Pradesh. The district lies towards north of the Ganga-Yamuna doab within the parallels 27°29' and 28°11' North latitude and 77°29' and 78°30' East latitude. The district is of fairly big size with an area of 1950 sq. miles. Its alluvial deposits have a gentle slope from North-West to South-East. There are several natural depressions apart from those formed by the river valleys and drainage lines. Topographically the district presents a trough like appearance with high Ganga and Yamuna banks at the extreme rims. It has a semi-desert type of climate, the Lang's factor for the district being 25.6 mm per °C and Meyer's N.S. Quotient 76. The soils of the district are alluvial with little leaching and considerable accumulation of salts on the surface. The alluvial beds varying from reddish brown to ash grey in colour pass through successive layers of sand, sandy-silt and clay with occasional compact beds of kankar of an indurated character. In some

places pisolitic small concretions of hydrated iron oxide are found disseminated in the soil beds.

Salt problem in Uttar Pradesh was recognised as early as 1876 and a commission was set up to investigate the deterioration of soils in Aligarh district where a vast area of over 3 million acres (about 15% of the total) consists of barren lands. Leather[10] (1876) showed that the injurious salts which were the decomposition products of igneous rocks under natural weathering processes and which caused damage were present in the soil profile itself and they become evident on the surface layers under certain conditions like a semi-arid climate, a hard kankar pan and temporary abundance of humidity interspersed with dry periods. He called such lands as 'Usar'. Soil factors in the district such a nearness of water table and or impedence of drainage due to the hard kankar pan caused an intensification in the area of 'Usar' patches. The 'Usar' reclamation committee[11] of Uttar Pradesh (1940) reported that the alkaline conditions in the soils of the district were mainly due to sodium carbonate and bicarbonate. The alkaline layers extended on a average to a depth of 3-4 feet. The distribution of saline soils, though comparatively less also covered a considerable area. These soils were characterised by the presence of sodium chloride and sodium sulphate and an open texture and existed in a state

of flocculation. The alkali soils could be classed as 'soloncts' and the saline soils as 'solon-chaks'.

According to the order of the genesis of the principal soil types, the district of Aligarh has been grouped into six natural soil regions as indicated on the attached soil map[12] of the district. (vide figure 4). The chief characteristics of these soils, as investigated till the time of undertaking the present work[13] are briefly indicated in tables I and II.

DIST. ALIGARH

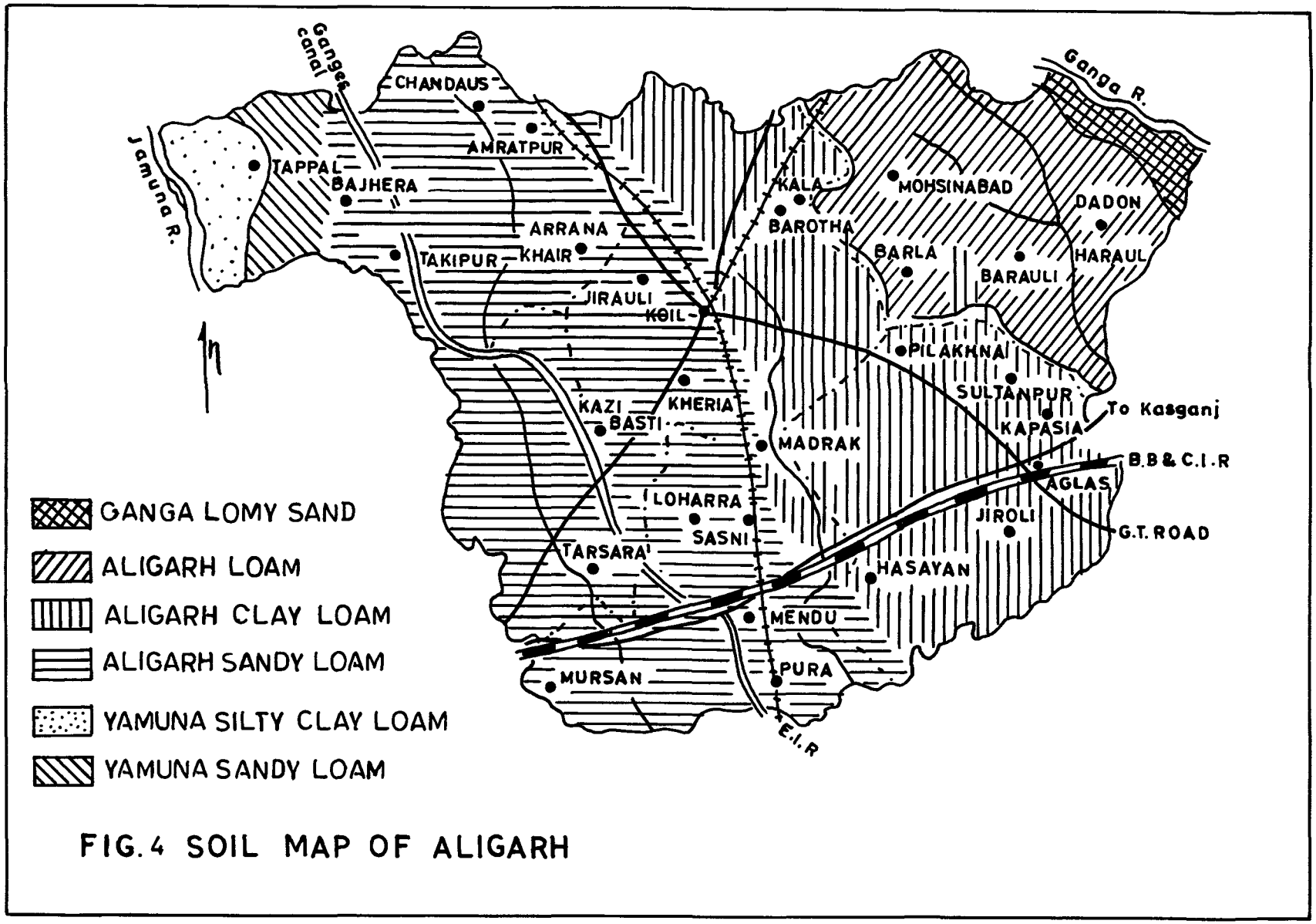

FIG. 4 SOIL MAP OF ALIGARH

Table I

Differential characteristics of soils from various regions of Aligarh District

Characteristics	Type I Ganga Khadir	Type II Eastern Uplands	Type III Central Lowlands
Profile development	Immature	Mature	Mature
Colour	Ash grey	Light brown	Whitish grey
Concretion	No	No	Thick kankar pan
Texture	Sandy to silty-loam	Sandy-loam, friable	Clayey loam, compact
Lime	High (slightly calcareous)	Low (non-calcareous)	High (Calcareous)
Soluble salts	High	Very low	High
Salt efflorescence	Present	Nil	Present
pH	7.8 and above	7.0	8.0
Clay	Very low	Moderate	High
Drainage	Imperfect	Good	Very poor
Water table	About 8 ft.	About 22 ft.	About 16 ft.
Main crops	Bajra, wheat, and barley	Jowar, maize, arhar, barley, wheat and pea	Sugarcane, barley and paddy

Table II

Differential characteristics of soils from various regions of Aligarh district

Characteristics	Type IV West Uplands	Type V Yamuna Khadir	Type VI Trans Yamuna Khadir
Profile development	Mature	Not fully	Mature
Colour	Reddish-brown	Dark-grey	Brownish grey
Concretion	No.	Kankar at bottom	Kankar at lower depth
Texture	Sandy loam	Clay	Loam
Time	Low, faintly alkaline	Rich, moderately calcareous	Average, non-calcareous
Soluble salts	Very low	Very high	Average
Salt efflorescence	Nil	Present	Not prominent
pH	7.0	8.0	7.0
Clay	Low	High	Moderate
Drainage	Excessive	Poor	Restricted
Water table	About 25 ft.	About 5 ft.	About 12 ft.
Main crops	Jowar, maize, barley, wheat and pea	Wheat or gram	Pea, barley & maize

Collection of soil samples

According to an axiom; analysis can be no better than the sample. This is all the more true in the collection of soil samples. The general problem of soil sampling has been summarised by the Association of Agricultural Chemists[14] as follows:

"In view of the variability of soils, it seems impossible to devise an entirely satisfactory method for sampling. It is obvious that the details of the procedure should be determined by the purpose for which the sample is taken."

During the collection of soil samples hereunder described, the importance of taking representative soil sample was kept in mind and variations in colour, texture, slope and cropping patterns were all adequately considered. The grass and other organic matter were removed from the surface. The different samples were collected from the area mentioned below up to the depth of 0 to 1·2 cm.

1. [illegible] - [illegible]

This soil is distributed in a narrow belt of recent alluvial tract of the Ganga in the north eastern corner of the district in tehsil Atrauli. The samples were collected

from the fields in the neighbourhood of Sankra bus-stand about two furlongs from the river bank.

2. [illegible] TYPE II - [illegible]

This soil covers almost the entire tehsil of Atrauli except for a thin strip of Ganga Khadir. The samples for the present work were collected from fields in village Datawali on the Aligarh Sankra Road.

3. [illegible] TYPE III - [illegible]

This soil occurs widely in the central low-lying tracts of the district in tehsil Koil and tehsil Sikandra Rao and is underlain by a thick pan of kankar, forming at some places a stiff impermeable sub-soil in the bottom layers. The samples were collected from the barren fields around the Aligarh University.

4. [illegible] TYPE IV - [illegible]

The soil is mainly distributed in the tehsils of Khair, Iglas and Jattari and forms numerous sandy ridges. The samples were collected from village Sodha.

5. [illegible] TYPE V - Yamuna khadir

The overflows of Yamuna in the extreme north-west

of the district has given rise to the formation of this soil in Tehsil Khair. The soil is hard with cloddy structure and gets puddled when wet. The samples were collected from the village Tappal situated on the bank of Yamuna river.

6. [illegible] - Khadir Yamuna alluvium

The tract of land containing this soil type lies parallel to the Yamuna khadir in the form of narrow belt about six miles wide. The soil is associated with kankar nodules and is slightly stiff. The samples were collected from Jattari village in tehsil Khair.

EXPERIMENTAL

ELECTRICAL CONDUCTIVITY

The electrical conductivity was measured at 30±1°C with the help of Phillips conductivity bridge and dip type cell. A 1 : 5 soil : water ratio suspension was used for the above purpose. The results obtained are recorded in tables III to VIII.

pH DETERMINATION

The pH was recorded with Elico pH meter model LI-10 with glass and saturated calomel electrode assembly. A 1 : 5 soil : water ratio suspension was used for measuring the pH of the soils. The results obtained are recorded in table III to VIII.

CATION EXCHANGE CAPACITY

The base exchange capacity of the soils was determined by titration by the method of Gangulí.[15] In this case a 5 gm. sample of the air dried soil was treated with 0.2 N HCl till acidic, shaken for half an hour and then filtered through Buchner funnel till the filtrate was free from chloride ions. The residue was transferred from the

Buchner funnel to a breaker and a suspension of known concentration prepared. It was then treated with the same volume of a saturated potassium chloride solution, shaken for half an hour, and left overnight. The exchanged acidity was titrated with standard 0.1N NaOH using phenolphthalein as indicator. From the amount of NaOH required, the b.e.c. of the soil was calculated. The results obtained for the base exchange capacity are recorded in tables III to VIII.

CaCO3 Calcium Content

The calcium carbonate content of the soils was determined by taking 10 grms of each of the sample on a Buchner funnel. The sample was washed with distilled water till free from chloride ions. It was then transferred to a conical flask, treated with 50 ml of 1N HCl, shaken and boiled on a steam bath till the reaction was over. It was then cooled to room temperature and back titrated with 1N NaOH using phenolphthalein as indicator. The end point was recorded when the pink colour persisted for 15 seconds on shaking the solutions. The results are recorded in tables III to VIII.

Trace and MT Determination

For trace elemental analysis samples were collected following described from typical soil profiles of Aligarh district. The following methods were adopted for the estimation of different elements.

Water soluble boron

Reagents: Curcumin-oxalic acid reagent (0.04 gm of finally grounded curcumin + 5 gram of oxalic acid in 95% ethanol), 95% ethanol and boron standards.

Procedure: For the estimation of water soluble boron,[16] 10 gram soil samples were weighed out in thimbles and the thimbles were then placed in the soxhlet assembly. Boron was then extracted with conductivity water heated in the flask below. The extract was transferred to a 100 ml flask in each case.

5 cc of the above solution was taken in a 100 cc boron free beaker, then 4 cc of curcumin oxalic acid reagent[17] was added and mixed well. Finally the solution was evaporated to dryness in an oven regulated at 55±3°C. A coloured substance, rosocyanine, developed during the evaporation and drying.

The beaker containing the dried residue was cooled to room temperature and the residue dissolved in 95% ethanol and filtered. The absorbance of the solution was recorded with Bausch and Lomb spectronic '20' at a wave length of 580 mu. A boron standard curve was similar prepared in the concentration range of 0 to 64 ppm vide figure 5, above 1. The results evaluated for water soluble boron are given in tables IX to XIV.

TOTAL COBALT

Reagents: 40% sodium citrate, perchloric acid, 2N NaCl, 1N HCl, 2N NaOH, 3% H_2O_2, 1-nitroso- 2 naphthol reagent, chloroform and cobalt standards.

Procedure: A 5 gram soil sample was digested with 5 cc of 60% per chloric acid and 20 cc of 1N HCl near to boiling point for 15 minutes and then filtered. The residue on the filter paper was carefully washed and the filtrate collected in a 50 cc volumetric flask and diluted to mark.

10 cc of the above extract was treated with 10 cc of sodium citrate solution and the pH adjusted to 3.5 with the help of 2N NaCl. To the solution 10 cc of 3% H_2O_2 was added and colour developed with 2 cc of 1-nitroso-2 naphthol solution. The colour was carefully extracted with 50 cc of chloroform. The chloroform layer[18] was washed with HCl and then with 2N NaOH.

The chloroform phase was utilised for taking absorbance measurement using Bausch and Lomb spectronic '20' at a wave length of 530 mu. A standard curve for cobalt was also prepared in the range of 0 to 70 ppm vide figure 5, curve 2. The results for total cobalt in Aligarh soil profiles are given in tables XV to XX.

<u>TOTAL and WATER SOLUBLE COPPER</u>

Reagents: Digestion mixture (100 cc of 60% $HClO_4$ + 10 cc of conc.H_2SO_4), conc. ammonia, 1% sodium diethyl dithiocarbamate, 25% ammonium chloride and copper standards in the case of TOTAL Copper.

Procedure: A 5 gram soil sample was taken and digested on a hot plate with 15 cc of digestion mixture or on orthophosphoric acid bath till the soil formed a clear white residue and almost all the perchloric acid had evaporated off. The residue was dissolved in water, filtered, and the volume of the filtrate made to 50 cc.

To 15 cc of the above solution, 5 cc of 25% ammonium chloride plus conc. ammonia were added till the solution became neutral to litmus and then 3 drops in excess were also added and the volume made up to 27 cc. The solution was centrifuged at 2000 r.p.m for 5 minutes.

10 cc of the above solution taken in 25 cc pyrex flask, was treated with 1 cc of sodium diethyl dithiocarbamate[19] solution and the volume made up to the mark. The colour absorbance of the solution was then recorded with Bausch and Lomb spectronic '20' at a wave length of 400 mμ. A standard curve was also drawn in the concentration range 0 to 80 ppm of copper vide figure 5, curve 3. The results

for total copper, evaluated from the standard curve, in Aligarh soil profiles are given in tables XXI to XXVI.

Available copper

Reagents: 1N ammonium acetate, 25% ammonia, neutral ammonium acetate of pH 7, 6N HCl, 1% solution diethyl dithiocarbamate and copper standards.

Procedure: To each of the 25 gms of air dried soil profile sample, weighed out in a 125 ml conical flask, 50 ml of 1N ammonium acetate was added. The flasks were stoppered and shaken for several minutes and allowed to stand overnight. The contents of the flask were then transferred to a 5.5 cm Buchner funnel in which a moist Whatmann filter paper No.42 had been seated by gentle suction. The soil was leached with 200 ml of ammonium acetate added in small quantities at a time so that the leaching process required at least an hour. The reagents blanks were run with the same volume of ammonium acetate. The leachate was then evaporated in a beaker.

The residue in the beaker was then wetted with 10 ml of 6N HCl, stirred with a police man and to bring the acid in good contact, and solution diluted with 15 ml redistilled water, followed by filtration to remove silica. The filtrate and the washings were collected in

100 ml volumetric flask and made up to volume at room temperature. 10 ml of each of the solutions were then utilised for the estimation of available copper as in the case of total copper. The results are recorded in tables XXVII to XXXII.

Total estimation : IRON

Reagents: Neutral 1M ammonium acetate, 1M ammonium acetate of pH 3, dil HCl, 1.5% ortho phenanthroline solution, 10% hydroxylamine hydrochloride solution and standard of iron.

Procedure: Total exchangeable iron was extracted with 1M ammonium acetate of pH 3. To avoid undue contact of the cold extractant with the soil, the entire process was completed within five minutes with the help of a filter pump. A total of 500 cc of the extractant was used for 25.0 gm of the soil in each case for extracting the element.

The filtrates were fumed on ammonium acetate by evaporation on a hot plate and the iron taken in solution with 1 cc, 1 N HCl and diluted to 5 cc with distilled water. 4 cc of the above solution in each case was used for the determination of iron colorimetrically using ortho phenanthroline as colour reagent.[20]

A standard curve was first drawn with the help of iron standards in the concentration range of 0 to 7 ppm

using Bausch and Lomb spectronic 20 for noting absorbance at a wavelength 490 mu. Iron was then determined in the extracts by first reducing the iron with dil HCl + a 10% solution of hydroxylamine hydrochloride and then adding 1 cc of orthophenanthroline reagent for colour development. Absorbance of the solutions was noted at 490 mu and the iron content in ppm evaluated from the standard curve vide figure 5, curve 4. The results for total exchangeable iron are given in tables XXXIII to XXXVIII.

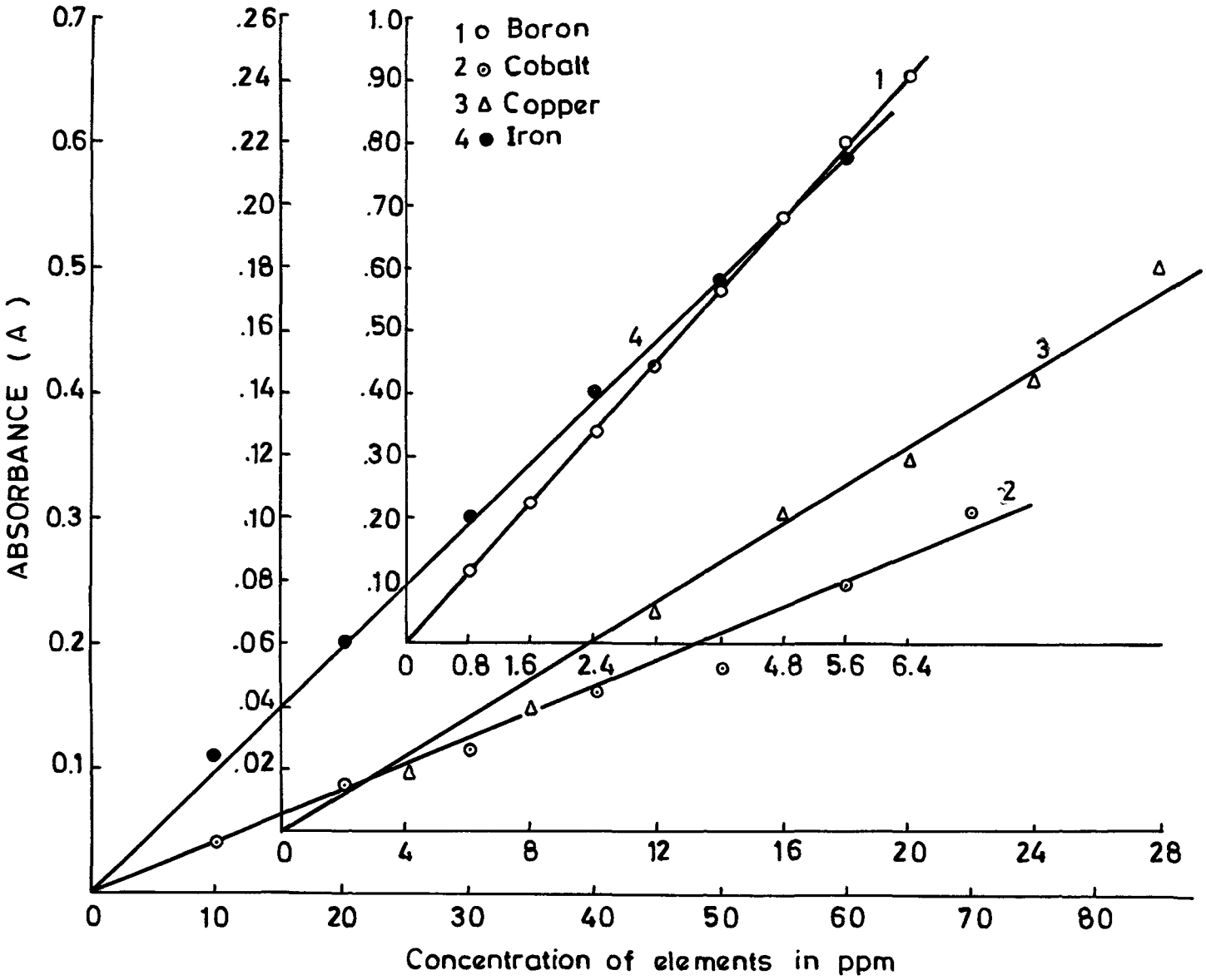

FIG. 5 STANDARD CURVES FOR B, Co, Cu and Fe USING SPECTROPHOTOMETRIC TECHNIQUE

Table III

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE I

Depth in cm	E.C./mhos/cm	pH	C.E.C./100 gm soil	% $CaCO_3$
0-28	0.2270	8.47	2.38	10.75
28-38	0.1575	8.10	1.59	10.13
38-43	0.1827	8.22	1.67	10.88
43-48	0.1731	8.12	1.67	9.64
48-91	0.1289	8.10	0.40	0.50

Table IV

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE II

Depth in cm	E.C./mhos/cm	pH	C.E.C./100 gm soil	% $CaCO_3$
0-18	0.1644	7.60	13.96	5.14
18-36	0.1289	7.95	11.50	5.76
36-58	0.1196	8.00	10.31	4.93
58-79	0.1241	8.10	12.37	4.50
79-97	0.1115	7.65	11.10	4.13
97-127	0.1230	7.85	26.01	4.01
127-168	0.1061	7.50	26.33	3.88

Table V

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE III

Depth in cm	E.C./mhos/cm	pH	C.E.C./100 gm soil	% $CaCo_3$
0-30	0.4699	9.35	20.62	9.16
30-61	3.2801	9.80	14.90	10.43
61-81	1.3100	8.72	5.00	45.64
81-114	1.9100	8.65	1.98	51.13
114-137	0.2860	8.37	1.90	53.76
137-152	0.1876	7.37	2.06	15.25
152-182	0.1686	7.50	1.11	14.63

Table VI

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE IV

Depth in cm	E.C./mhos cm	pH	C.E.C./100 gm soil	% $CaCO_3$
0-28	0.1174	8.15	9.86	8.01
28-63	0.1134	7.60	9.99	6.00
63-96	0.9982	8.07	2.21	4.86
96-135	0.5487	8.55	13.54	4.50
135-182	0.6578	8.52	14.75	4.38

Table VII

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE V

Depth in cm	E.C./mhos cm	pH	C.E.C./100 gm soil	% $CaCo_3$
0-28	0.4385	8.85	3.25	9.00
28-58	0.6578	9.95	3.33	10.01
58-94	0.0109	9.65	5.53	10.26
94-112	0.0082	9.50	4.40	9.25

Table VIII

Physico-chemical characteristics of the soils of Aligarh District

SOIL TYPE VI

Depth in cm	E.C./mhos/cm	pH	C.E.C./100 gm soil	% $CaCo_3$
0-30	0.0657	8.00	15.46	6.65
30-58	0.0597	7.95	22.28	3.88
58-92	0.5296	8.45	4.92	20.05
92-147	0.2990	8.45	4.72	25.93

Table IX

Estimation of water soluble boron in Aligarh soils profiles by spectrophotometric (curcumin-oxalic acid) method

SOIL TYPE I

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron reading from standard curve	Boron in ppm
0-28		0.490	3.46	6.92
28-38		0.485	3.45	6.90
38-43	580 mu	0.480	3.40	6.80
43-48		0.375	2.64	5.28
48-91		0.260	1.84	3.68

Table X

Estimation of water soluble boron in Alipur soils profiles by spectrophotometric (curcumin-oxalic acid) method

SOIL TYPE II

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron read-ing from standard curve	Boron in ppm
0-18		0.20	1.40	2.80
18-36		0.23	1.64	3.28
36-58		0.17	1.20	2.40
58-79	500 mu	0.09	0.64	1.28
79-97		0.04	0.30	0.60
97-127		0.08	0.58	1.16
127-168		0.11	0.80	1.60

Table XI

Estimation of water soluble boron in Alfisol soil profiles by spectrophotometric (curcumin-oxalic acid) method

SOIL TYPE III

Concentration of soil in the extract = 0.5 gm/5ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron read-in from standard curve	Boron in µg
0-30		0.400	2.00	3.64
30-61		0.245	1.74	3.48
61-81		0.520	3.68	7.36
81-114	560 mu	0.415	2.88	5.76
114-137		0.700	4.96	9.92
137-152		0.675	4.80	9.60
152-182		0.510	3.60	7.20

Table XII

Estimation of water soluble boron in Alfisols soils profiles by spectrophotometric (curcumin-oxalic acid) method

Soil type IV

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron read-ing from standard curve	Boron in ppm
0-28		0.460	3.24	6.48
28-63		0.810	5.74	11.48
63-96	580 mu	0.580	4.09	8.18
96-135		0.320	2.26	4.52
135-182		0.185	1.32	2.64

Table XIII

Estimation of water soluble boron in Alfisols soils profiles by spectrophotometric (curcumin-oxalic acid) method

Soil Type V

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron reading from standard curve	Boron in p.p.m
0-28		0.165	1.32	2.64
28-58		0.250	1.76	3.52
58-94	530 mu	0.140	1.00	2.00
94-112		0.365	2.60	5.20

Table XIV

Estimation of water soluble boron in Alipoah soils profiles by spectrophotometric (curcumin-oxalic acid) method

SOIL TYPE VI

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of curcumin oxalic acid reagent = 4.0 ml

Depth in cm	Wave length used	Absorbance	Boron reading from standard curve	Boron in ppm
0-30		0.130	0.92	1.84
30-58		0.170	1.20	2.40
58-92	500 mu	0.195	1.40	2.80
92-147		0.125	0.88	1.76

Table XV

Estimation of total cobalt in Alwarh soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL TYPE I

Concentration of soil in the extract = 1.0 gm/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt reading from standard curve	Total cobalt in µg
0-28		0.065	16.00	16.00
28-38		0.060	15.00	15.00
38-43	530 mu	0.050	12.50	12.50
43-48		0.040	10.00	10.00
48-91		0.000	0.00	0.00

Table XVI

Estimation of total cobalt in Alipur soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL XVIII

Concentration of soil in the extract = 1.0 gm/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt reading from standard curve	Total cobalt in ppm
0-18		0.010	3.00	3.00
18-36		0.015	4.00	4.00
36-79	530 mu	0.100	3.00	3.00
79-97		0.005	1.50	1.50
97-127		0.400	10.00	10.00
127-168		0.250	61.50	61.50

Table XVII

Estimation of total cobalt in Alipur soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL TYPE III

Concentration of soil in the extract = 1.0 gm/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt reading from standard curve	Total cobalt in ppm
0-30		0.130	32.50	32.50
30-61		0.140	33.50	33.50
61-81		0.145	34.00	34.00
81-114	530 mu	0.055	15.00	15.00
114-137		0.080	19.00	19.00
137-152		0.090	22.00	22.00
152-182		0.100	25.00	25.00

Table XVIII

Estimation of total cobalt in Aligarh soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL TYPE IV

Concentration of soil in the extract = 1.0 µg/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt reading from standard curve	Total cobalt in µg
0-28		0.050	12.50	12.50
28-63		0.075	18.50	18.50
63-96	530 mu	0.085	20.50	20.50
96-135		0.080	19.00	19.00
135-162		0.055	5.00	5.00

Table XLX

Estimation of total cobalt in Aligarh soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL TYPE V

Concentration of soil in the extract = 1.0 gm/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt read-ing from standard curve	Total cobalt in ppm
0-28		0.040	10.00	10.00
28-58	530 mu	0.060	15.00	15.00
58-94		0.120	31.00	31.00
94-112		0.100	25.00	25.00

Table XX

Estimation of total cobalt in Aligarh soil profiles by spectrophotometric (1-nitroso-2 naphthol) method

SOIL [illegible] VI

Concentration of coil in the extract = 1.0 µg/10 ml

Volume of solution used = 10.0 ml

Colour extracted with = Chloroform

Depth in cm	Wave length used	Absorbance	Cobalt reading from standard curve	Total cobalt in ppm
0-30		0.170	42.00	42.00
30-58	530 mu	0.220	53.00	53.00
58-92		0.200	50.00	50.00
92-147		0.260	64.00	64.00

Table XXI

Estimation of total copper in Allsorb soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE I

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Con. of soil extract in gms/10 ml	Wave length used	Absorbance	Copper reading from standard curve	Total copper in ppm
0-28	0.5183		0.0550	9.50	48.81
28-38	0.5013		0.0575	9.75	48.62
38-43	0.5014	440 mu	0.0575	9.75	48.60
43-48	0.5016		0.0575	9.75	48.58
48-91	0.5017		0.0400	7.00	34.87

Table XXII

Estimation of total copper in Alikarh soil profiles by spectrophotometric (Sodium diethyl dithiocarbamate) method

SOIL TYPE II

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in	Conc.of soil extract in gms/10 ml	Wave length	Absorbance	Copper reading from standard curve	Total copper in ppm
0-18	0.5208		0.0400	7.00	33.59
18-36	0.4846		0.0650	11.00	56.74
36-58	0.4677		0.0500	8.50	45.43
58-79	0.4685	440 mu	0.0600	10.00	53.36
79-97	0.4981		0.0475	8.00	40.15
97-127	0.4532		0.0600	10.00	54.56
127-168	0.5582		0.0750	12.50	57.55

Table XXIII

Estimation of total copper in Alfisol soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE III

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in	Con. of soil extractin gms/10 ml	Wave length used	Absorbance	Copper reading from standard curve	Total copper in ppm
0-30	0.4993		0.0550	9.50	47.51
30-61	0.5048		0.0500	8.50	42.09
61-81	0.5218		0.0675	11.50	55.09
81-114	0.4693	440 mu	0.0550	9.50	50.61
114-137	0.5312		0.0600	10.00	47.06
137-152	0.4826		0.0400	7.00	36.26
152-162	0.5473		0.0400	7.00	31.97

Table XXIV

Estimation of total copper in Alicarh soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE IV

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Con. of soil extract in gms/10 ml	Wave length used	Absorbance	Copper reading from standard curve	Total copper in ppm
0-28	0.5566		0.070	12.00	53.81
28-63	0.5448		0.075	12.50	57.35
63-96	0.4653	440 mu	0.060	10.00	53.72
96-135	0.3670		0.065	11.00	58.88
135-182	0.4707		0.055	9.50	50.43

Table XXV

Estimation of total copper in Aliyarh soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE V

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Conc. of soil extract in gms/10 ml	Wave length used	Absorbance	Copper reading from standard curve	Total copper in ppm
0-28	0.5215		0.0550	9.50	45.15
28-58	0.5180	440 mu	0.0675	11.50	58.61
58-94	0.4821		0.0550	9.50	47.57
94-112	0.4082		0.0600	10.00	50.86

Table XXVI

Estimation of total copper in Alluvial soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE VI

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Conc. of soil extract in gms/10 ml	Wave length used	Absorbance	Copper reading from Standard curve	Total copper in p.p.m
0-30	0.5215		0.0600	10.00	47.91
30-58	0.5180	440 mu	0.0625	10.50	50.67
58-92	0.4821		0.0700	12.50	60.01
92-147	0.4882		0.0575	9.75	49.92

Table XXVII

Estimation of available copper in Alfisols soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE I

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper reading from standard curve	Available copper in ppm
0-28		0.010	2.0	1.00
28-38		0.005	1.0	0.50
38-43	440 mu	0.010	2.0	1.00
43-48		0.000	0.0	0.00
48-91		0.000	0.0	0.00

Table -XVIII

Estimation of available copper in Ali ash soil profile by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE II

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper recording from standard curve	Available copper in ppm
0-18		0.0100	2.0	1.00
18-36		0.0175	2.9	1.45
36-58		0.0100	2.0	1.00
58-79	440 mu	0.0125	2.4	1.20
79-97		0.0125	2.4	1.20
97-127		0.0050	1.0	0.50
127-168		0.0275	4.5	2.25

Table XXIX

Estimation of available copper in Alfisol soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE III

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper reading from standard curve	Available copper in ppm
0-30		0.0100	2.0	1.00
30-61		0.0075	1.5	0.75
61-81		0.0055	1.0	0.50
81-114	440 mu	0.0275	4.5	2.30
114-137		0.0150	2.9	1.85
137-152		0.0125	2.4	1.20
152-182		0.0100	2.0	1.00

Table XXX

Estimation of available copper in Aligarh soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL PROFILE IV

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper reading from standard curve	Available copper in ppm
0-28		0.0175	2.9	1.45
28-63		0.0175	2.9	1.45
63-96	440 mu	0.0100	2.0	1.00
96-135		0.0600	9.0	4.50
135-182		0.0150	2.5	1.25

Table XXXI

Estimation of available copper in Alfisols soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE V

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper reading from standard curve	Available copper in ppm
0-28	440 mu	0.025	4.5	2.25
28-58		0.005	1.0	0.25
58-94		0.005	1.0	0.50
94-112		0.010	2.0	1.00

Table XXXII

Estimation of available copper in Aligarh soil profiles by spectrophotometric (sodium diethyl dithiocarbamate) method

SOIL TYPE VI

Concentration of soil in the extract = 2.0 gm/10 ml

Volume of extract used = 10.0 ml

Volume of 2% sodium diethyl dithiocarbamate = 1.0 ml

Volume of concentrated ammonia added = 5.0 ml

Depth in cm	Wave length used	Absorbance	Copper reading from standard curve	Available copper in ppm
0-30	440 mu	0.0025	0.5	0.25
30-58		0.0050	1.0	0.50
58-92		0.0025	0.5	0.25
92-147		0.0050	1.0	0.50

Table XXXIII

Estimation of total exchangeable iron in Aliyarh soil profiles by spectrophotometric (orthophenon-throline) method.

SOIL TYPE I

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of hydroxylamine hydrochloride = 2.0 ml

Volume of 1.5% orthophenonthroline = 1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-28		0.370	37.0	74.00
28-38		0.500	50.0	100.00
38-43	490 mu	0.480	48.0	96.00
43-48		0.550	55.0	110.00
48-91		0.585	58.5	117.00

Table XXXIV

Estimation of total exchangeable iron in Aligarh soil profiles by spectrophotometric (orthophenonthroline) method.

SOIL TYPE II

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of hydroxylamine hydrochloride = 2.0 ml

Volume of 1.5% orthophenonthroline = 1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-18		0.025	2.50	5.00
18-36		0.240	24.00	48.00
36-58	490 mu	0.160	16.00	32.00
58-79		0.030	3.00	6.00
79-97		0.490	49.00	98.00
97-127		0.310	31.00	62.00
127-168		0.185	18.50	37.00

Table XXXV

Estimation of total exchangeable iron in Alicarh soil profiles by spectrophotometric (orthophenanthroline) method.

SOIL TYPE III

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of hydroxylamine hydrochloride = 2.0 ml

Volume of 1.5% orthophenanthroline = 1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-30		0.43	43.0	86.00
30-61		0.32	32.0	64.00
61-81		0.30	30.0	60.00
81-114	490 mu	0.44	44.0	88.00
114-137		0.45	45.0	90.00
137-152		0.20	20.0	40.00
152-182		0.10	10.0	20.00

Table XXXVI

Estimation of total exchangeable iron in Aligarh soil profiles by spectrophotometric (orthophenonthroline) method

SOIL TYPE IV

Concentration of soil in the extract	=	0.5 gm/5 ml
Volume of extract used	=	5.0 ml
Volume of hydroxylamine hydrochloride	=	2.0 ml
Volume of 1.5% orthophenonthroline	=	1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-28		0.175	17.50	35.00
28-63		0.140	14.00	28.00
63-96	490 mu	0.070	7.00	14.00
96-135		0.420	42.00	84.00
135-182		0.110	11.00	22.00

Table XXXVII

Estimation of total exchangeable iron in Alicarh soil profiles by spectrophotometric (orthophenanthroline) method

SOIL TYPE V

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of hydroxylamine hydrochloride = 2.0 ml

Volume of 1.5% orthophenonthroline = 1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-28		0.5500	55.00	110.00
28-58	490 mu	0.0000	8.00	16.00
58-94		0.0475	4.75	9.00
94-112		0.4600	46.00	92.00

Table XXXVIII

Estimation of total exchangeable iron in Aligarh soil profiles by spectrophotometric (orthophenanthroline) method.

SOIL TYPE VI

Concentration of soil in the extract = 0.5 gm/5 ml

Volume of extract used = 5.0 ml

Volume of hydroxylamine hydrochloride = 2.0 ml

Volume of 1.5% orthophenonthroline = 1.0 ml

Depth in cm	Wave length used	Absorbance	Iron reading from standard curve	Total exchangeable iron in ppm
0-30		0.06	6.00	12.00
30-58	490 mu	0.31	31.00	62.00
58-92		0.10	10.00	20.00
92-147		0.48	48.00	96.00

RESULTS AND DISCUSSION

The data on pH, electrical conductivity and calcium carbonate content of the six profiles vide tables III to IX indicate that Aligarh soils are mostly sodic saline and calcareous. The calcium carbonate content has been found to increase with depth in profiles III, V and VI and decrease with depth in I, II and IV. Particularly intense calcareous conditions and alkalisation are apparent in soil type III. The texture of the soils has been found to vary from clay to sandy loam.

A reference to tables IX to XIV indicates that the water soluble boron content of the soils varies from 0.60 ppm to 11.40 ppm with an average of 4.5 ppm for the district. According to Reeves et al;[21] 0.55 ppm is the dividing line for water soluble boron in case of normal and deficient soils while Richards[22] has reported a concentration ~~and reported a concentration~~ below 0.70 ppm as safe for sensitive plants, 0.70 ppm to 1.05 ppm as marginal and >1.50 ppm as unsafe. On the basis of the above scale boron content of the soils is towards higher limits. Analysis of the well water from the areas of different soil types is given in table XXIA. It may be a source of the high proportion of boron in the soils. Boron is particu-

larly high in soil profiles I, III and IV which also show poor permeability. pH has been found to have no relationship with the boron content of the soils ($r = -0.000$). The authors could also find no relationship between electrical conductivity and boron content of the soil ($r = -0.002$). Variation of boron with cation exchange capacity is, however, quite significant ($r = -0.41$). A significant positive correlation is observed between the calcium carbonate content of the soils and water soluble boron. This is in accordance with the observations of Mathur et.al.[23] on Rajasthan soils. It is possible that calcium carbonate may be a factor which may have caused accumulation of large amounts of boron in Aligarh soil profiles.

The total cobalt content of the soils varied from 0.0 ppm to 64 ppm with an average of 21.12 ppm for all the profiles and from 3 ppm to 42 ppm in case of surface samples with an average of 19.33 ppm. Singh and Singh[24] have reported values ranging from 0.6 ppm to 20.1 ppm in some of the soils of Uttar Pradesh. A limit of less than 2.5 ppm has been found to be very deficient for crop growth and critical deficiency by Walsh et al, 2.5 ppm to 5 ppm moderately deficient and above 5.0 ppm satisfactory. The cobalt range of the soils is thus well over the deficiency limit. Except in soil profile I where it decreases with depth total cobalt has been found to exhibit

no definite order of distribution with depth. A large accumulation of cobalt is seen in the deep layers of soil types II, V and VI and in the uppermost layers of soil types I and III. Analysis of the data on the basis of correlation coefficients reveals that although total cobalt exhibits significant correlations with calcium carbonate content of the soils and their cation exchange capacity, no such relationship is available in case of pH or the electrical conductivity. The results are in accordance with the observations of Bodrio[25] on calcium carbonate and those of Reddy and Mehta[26] on pH but in variance with those of Singh and Singh (loc.cit.). A reference to the analysis of irrigation water (vide Table XXXIX) reveals that the source of cobalt in the soils is unrelated with irrigation water.

The data on total and available copper (vide tables XXVII to XXXII) show that out of the total copper only about 2% of it, on an average, is in available form. The cause of the low availability of copper may be a deficiency of soluble complexing agents in soil that can release copper. Copper requirement of plants varies from crop to crop. Lundbald et al[27] have reported 7.0 ppm as the dividing line for deficiency of total copper, while Piper[28] suggests 0.5 ppm as the limit for available copper. On the basis of these findings, available copper of about 15% of the soil samples is below the requirement. These

soils belong to types I and II and happen to be 'khadir' lands. Statistical analysis of the results of investigation on copper yield a significant positive correlation ($r = 0.510$ for available copper and $r = 0.788$ for total copper) between copper content and the cation exchange capacity of the soil although no such relationship is observed in case of pH, electrical conductivity and percentage of calcium carbonate. Contradictory findings on correlation coefficients between pH, electrical conductivity, calcium carbonate content and available copper have been made by different workers[29,30,31,32] and hence no definite conclusion could be drawn on the relationship between the physico-chemical properties of the soil and copper availability.

There is a substantial variation in the total exchangeable iron content of the soil profiles. An accurate estimation of the ferrous form of iron in the above samples could not be done due to oxidation of the same on storage of the samples. Preliminary experiments, however, indicated that a considerable part of the total exchangeable iron exists in ferric or precipated state and hence is unavailable to plants. This seems to be the result of calcareous and alkaline conditions in the soil. An examination of the correlation coefficients between iron and the physico-chemical properties of the

Table XXXIX

Trace Element Status of the Irrigation Waters of Different Soil Types

Soil type	Micronutrient				
	Boron	Cobalt	Total copper	Available copper	Total exchangeable iron
I	0.042	0.000	Nil	Nil	Nil
II	0.025	0.000	"	"	"
III	0.025	0.000	"	"	"
IV	0.030	0.005	"	"	"
V	0.050	0.000	"	"	"
VI	0.063	0.000	"	"	"

Table XL

Correlation Coefficients between Physico-chemical Properties of the Soils and the Trace Elements.

Micronutrient	E.C.	pH	C.E.C.	$CaCo_3$
Water soluble boron	- 0.002	0.000	- 0.410	0.350
Total cobalt	- 0.012	0.000	0.630	0.450
Total copper	- 0.045	- 0.080	0.510	0.090
Available copper	0.009	- 0.150	0.790	0.024
Total exchangeable iron	- 0.050	0.044	- 0.260	0.180

Table XLI

Correlation Coefficients between trace* elements in the soils

Micronutrient	Boron	Cobal	Total copper	Available copper	Total exchangeable iron
Water soluble boron	-	0.0790	0.1519	0.0862	0.0199
Total cobalt	0.0790	-	0.4380	0.0790	0.6728
Total copper	0.1519	0.4380	-	0.0300	0.0720
Available copper	0.0862	0.0790	0.0800	-	0.0115
Total exchangeable iron	0.0199	0.6728	0.0720	0.0115	-

(*At 5% level of significance and 30 d.f. the tabulated value of t is equal to 2.042).

soil indicates that at 5% level there is no significant correlation between total exchangeable iron and the variables and it may be that the integrated effect of all of them determines the range of iron in the soil. This is in agreement with findings of some workers[39] who have reported inconsistent results for iron on the soils of Punjab.

Attempt in finding correlations between the different trace elements in the soils revealed (vide table XLI) that significant positive correlations exist between boron and available copper; cobalt and total copper as well as cobalt and exchangeable iron. No such relationship is observed in other cases.

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Chapter XIX

A Physico-Chemical Study of the Modifications of Nicotine in Tobacco.

A Physico-Chemical Study Of the Interactions Of Nicotine With Montmorillonite.

Studies on clays have revealed that they interact with many organic compounds. Some of these interactions are highly significant and workers have devoted a considerable part of their attention to clay organic complexes[1,2,3]. Adsorption isotherms have been extensively used to explain some of the interactions.[4,5] Work[6,7] in these laboratories has revealed that nicotine and some heterocyclics can be successfully used for the electrometric titrations of acid clays and that the interactions are often stoichiometric. Inspite of the study, the mechanism of these interactions is, in most cases, doubtful. The confusion probably arises as a result of the existence of several chemically active heterogeneous sites on the edges and lateral surfaces of clays which are available for interaction and the simultaneous interferences that often arise from environmental factors during these interactions.

Montmorillonite occurs abundantly in the peninsular soils of India. The use of nicotine and other heterocyclics has been suggested as pesticides. The importance of nicotine in the functions of the central nervous system is well known

at the present time. The utility of the physico-chemical investigations on the interactions of nicotine with montmorillonite, with particular reference to adsorption and desorption of nicotine in clays, therefore, cannot be overemphasized.

The objectives of the present study were to investigate the adsorption of nicotine on acid and base saturated montmorillonites and thereby obtain information on the possible mechanism of adsorption and interaction of montmorillonites with nicotine.

EXPERIMENTAL

The clay mineral used in these investigations was montmorillonite, collected by Dr.Ralph J.Hosser and verified under his direction in the mineralogical laboratories of the Columbia University by comparison with the original sample from Amori, Mississippi. It was a monomineralic sample of the American Petroleum Institute's Project No.49. The sample was obtained from Wards Natural Science Establishment,Inc., Rochester,U.S.A. It was broken up in a mortar using a rubber covered pestle. The organic matter was oxidised with hydrogen peroxide and the mixture diluted with distilled water. The clay was then dispersed by electrical stirring. The suspension obtained was passed

through sheets of Whatmann filter paper filled in the bowl of "International Chemical" centrifuge at a speed of 3500 r.p.m to remove any coarse matter. The suspension consisted of $< 2\mu$ clay particles.

Preparation of Na-montmorillonite

The clay suspension was then treated with sodium chloride and dilute hydrochloric acid till the concentration of the supernatant liquid was 2N with respect to sodium-chloride and 0.1N with respect to hydrochloric acid. The mixture was shaken for half an hour after which the supernatant acid salt solution was removed from the clay suspension by decantation. This treatment was repeated three times and the sodium clay suspension then freed from chloride ions till the clay dispersed and till the conductivity of the suspension was of the same order as that of distilled water 10^{-5} mhos/cm. The suspension was stored in pyrex glassware and used when required.

Preparation of hydrogen saturated montmorillonite

Hydrogen saturated clay with minimal aluminium was freshly prepared vide Aldrich and Buchanan's method[6] from the suspension by passing it through a column of H-Dowex-50w-X8 cation exchange resin at a speed of 3 cc per minute

till the pH and conductance of the suspension became constant. It was then quickly used for potentiometric and conductometric titrations as well as adsorption experiments to avoid any ageing or decomposition of the hydrogen clay. The concentration of the suspension varied from 0.802 to 1.324 gm per 100 ml of water.

Preparation of Al^{+3}, Ca^{+2}, Ba^{+2} and NH_4^+ montmorillonites

To obtain the aluminium, calcium, barium and ammonium montmorillonites, the sodium clay suspension was treated three times with normal aluminium chloride solution in the case of aluminium clay; calcium chloride solution in the case of calcium clay; barium chloride solution in the case of barium clay; and ammonium chloride solution in the case of ammonium clay. The suspensions were then washed with distilled water till the resistance in each case was of the same order as that of distilled water (10^{-5} mhos/cm). The suspensions contained approximately 1.2 to 2.5g of clay per 100 ml of water in each case.

Determination of concentration of suspensions

The concentration of each of the suspensions used for adsorption experiments was determined by evaporating 5 ml of each of the suspension in a petri dish of known

weight and drying the residue at 105°C and finally determining the weight of the residue.

Preparation of nicotine and other solutions

Nicotine was purified by distilling it at a temperature of 98°C and 4 mm pressure in an inert atmosphere. A standard solution of nicotine was then prepared by dissolving 0.50 gm of nicotine and making up the solution to 100 ml with double distilled water. Since the solution had a tendency to undergo decomposition, it was freshly prepared everytime before use.

A standard solution of hydrochloric acid of the same strength as nicotine was also prepared as per the usual method.

Set 1.

POTENTIOMETRIC AND CONDUCTOMETRIC TITRATIONS

Freshly prepared samples of acid saturated montmorillonites and base saturated montmorillonites were used for potentiometric and conductometric studies. The time interval between the preparation of hydrogen saturated montmorillonite and each titration was kept as minimum and uniform as possible to avoid the effects of aluminium movements in hydrogen clay saturated montmorillonite.

Standard solution of sodium hydroxide was used as titrant in case of hydrogen saturated montmorillonite. To titrate it 5 cc of the suspension was taken in several pyrex glass tubes. To each of these tubes varying amounts of 0.103N NaOH were added and the suspensions stirred occasionally for three hours before recording pH and conductance.

To titrate acid and base saturated montmorillonite suspensions; standard nicotine solution was used as titrant. To 5.0 cc of each of the suspensions taken in a number pyrex glass tubes varying amounts of 0.03N nicotine sodium were added and the suspensions stirred occasionally for three hours before recording pH and conductance. The stirring time and total time for all the titrations was kept as uniform as possible.

The pH readings were recorded with Beckman pH meter model G, with saturated calomel and glass electrode assembly. Conductivity measurements were carried out with the help of Philip's conductivity meter with dip type cell.

The cation exchange capacity values of the clays and their binary mixtures were evaluated from the inflection points in their titration curves. These values were further verified by the acetate method[9] and the KCl-KOH method.[10]

The results obtained for pH and conductivity measurements with sodium hydroxide are given in table XLII and represented vide figures 6 and 8, curves 1 and 1 respectively. Similarly the results obtained for pH and conductivity measurements of acid and base saturated montmorillonites with nicotine are given in tables XLIII to XLVIII and represented vide figures 6 to 9.

Set 1.

Table XLII

Potentiometric and conductometric titrations of hydrogen saturated montmorillonite with sodium hydroxide.

Concentration of clay = 0.0534 gms/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of NaOH = $\frac{N}{30}$

Volume of NaOH added in cc	Volume of water added in cc	Meq of NaOH per 100 gm of clay	pH of the mixture	Conductance x 10^3 mhos
0.0	15.0	0.000	3.20	4.40
0.1	14.9	6.242	3.35	3.33
0.2	14.8	12.484	3.65	3.03
0.5	14.5	31.210	4.80	1.95
0.8	14.2	49.936	6.05	1.30
1.2	13.8	74.904	7.35	1.15
1.4	13.6	87.388	8.00	1.05
1.6	13.4	99.872	8.15	1.05
1.8	13.2	112.356	8.30	2.10
2.0	13.0	124.840	8.45	5.25
2.2	12.8	137.324	8.60	5.95
2.5	12.5	156.050	8.65	7.99
3.0	12.0	187.260	8.75	8.93
3.5	11.5	218.470	8.85	10.85
4.0	11.0	249.680	8.85	18.11
4.5	10.5	280.890	8.90	20.00

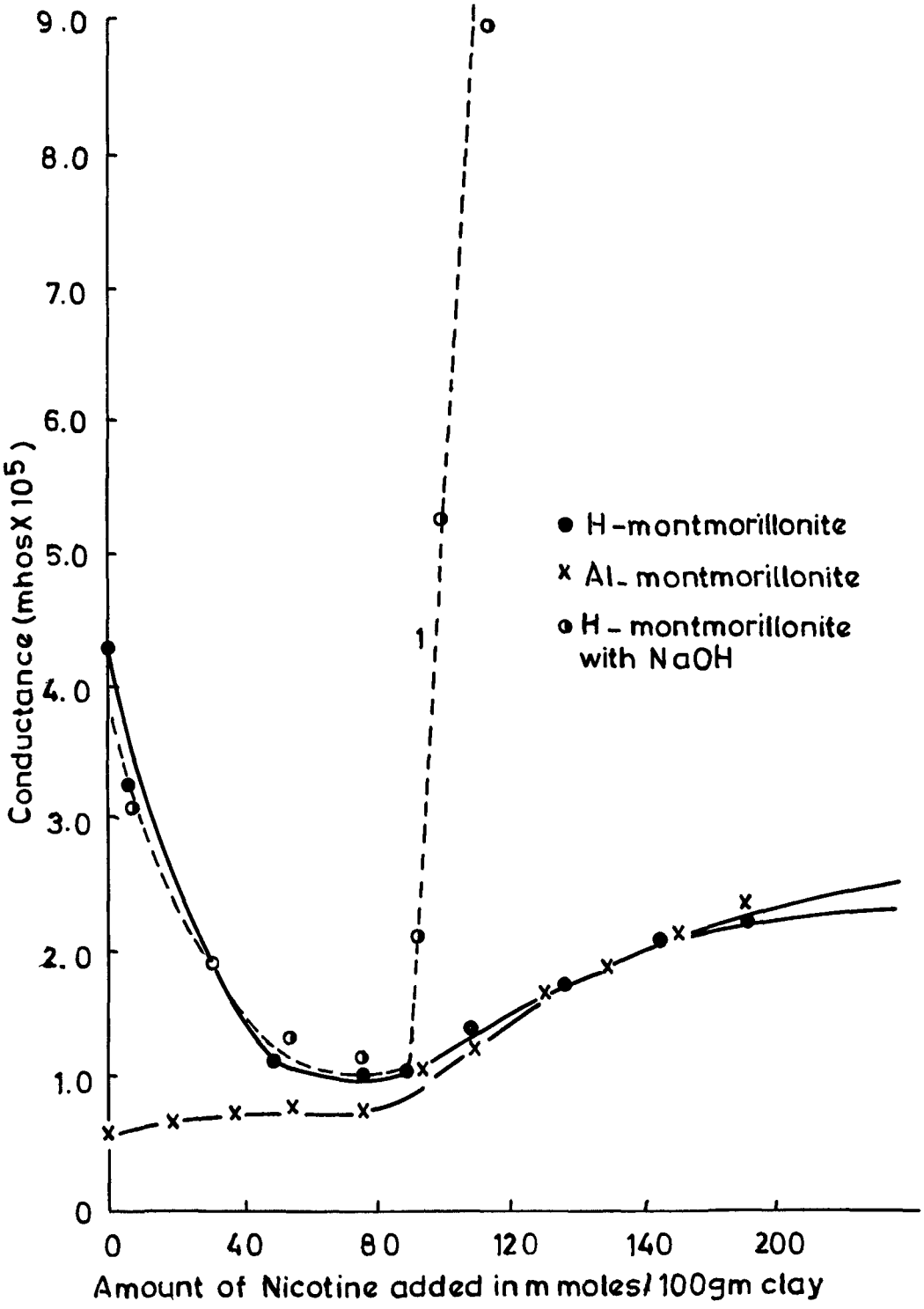


Fig. 6 Conductometric titrations of hydrogen and aluminium saturated montmorillonites (The dotted curve is for conductometric titration of H-montmorillonite with NaOH)

Table XLIII

Potentiometric and conductometric titrations of hydrogen saturated montmorillonite with nicotine

Concentration of clay = 0.0534 gms/5 ml

Volume of clay suspension taken in different tubes = 5.0 ml

Strength of nicotine = 0.03N

Volume of nicotine in ml	Volume of water added in ml	Meq. of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	15.00	0.000	3.20	4.25
0.1	14.90	6.242	3.60	3.25
0.2	14.80	12.484	4.25	3.05
0.5	14.50	31.210	4.90	1.92
0.8	14.20	49.936	5.50	1.27
1.2	13.80	74.904	6.00	1.05
1.4	13.60	87.388	6.40	1.05
1.6	13.40	99.872	6.85	1.40
1.8	13.20	112.356	7.40	1.70
2.0	13.00	124.840	7.95	2.05
2.2	12.80	137.324	8.10	2.20
3.0	12.00	187.260	8.35	2.25
3.5	11.50	218.470	8.60	2.30
4.0	11.00	249.680	8.75	2.35
5.0	10.00	312.100	8.80	2.60
6.0	9.00	347.520	8.80	2.90
7.0	8.00	436.940	8.85	3.00

Table XLIV

Potentiometric and conductometric titrations of aluminium saturated montmorillonite with nicotine

Concentration of clay = 0.0656 gms/5 ml suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = 0.03 N

Volume of nicotine in cc	Volume of water added in cc	Meq of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^{5} mhos
0.0	20.0	0.00	4.10	0.598
0.4	19.6	18.77	4.20	0.657
0.8	19.2	37.54	4.50	0.751
1.2	18.8	56.31	4.70	0.822
1.6	18.4	75.08	5.25	0.751
2.0	18.0	93.85	5.50	1.020
2.4	17.6	112.62	5.75	1.310
2.8	17.2	131.39	6.05	1.640
3.2	16.8	150.16	6.70	1.820
3.6	16.4	168.93	7.25	2.050
4.0	16.0	187.70	7.30	2.260
5.0	15.0	234.74	7.60	2.430
6.0	14.0	281.73	7.75	2.740
7.0	13.0	328.63	7.80	2.980
8.0	12.0	375.40	7.95	3.250
9.0	11.0	422.53	8.10	3.470
10.0	10.0	469.48	8.20	3.650

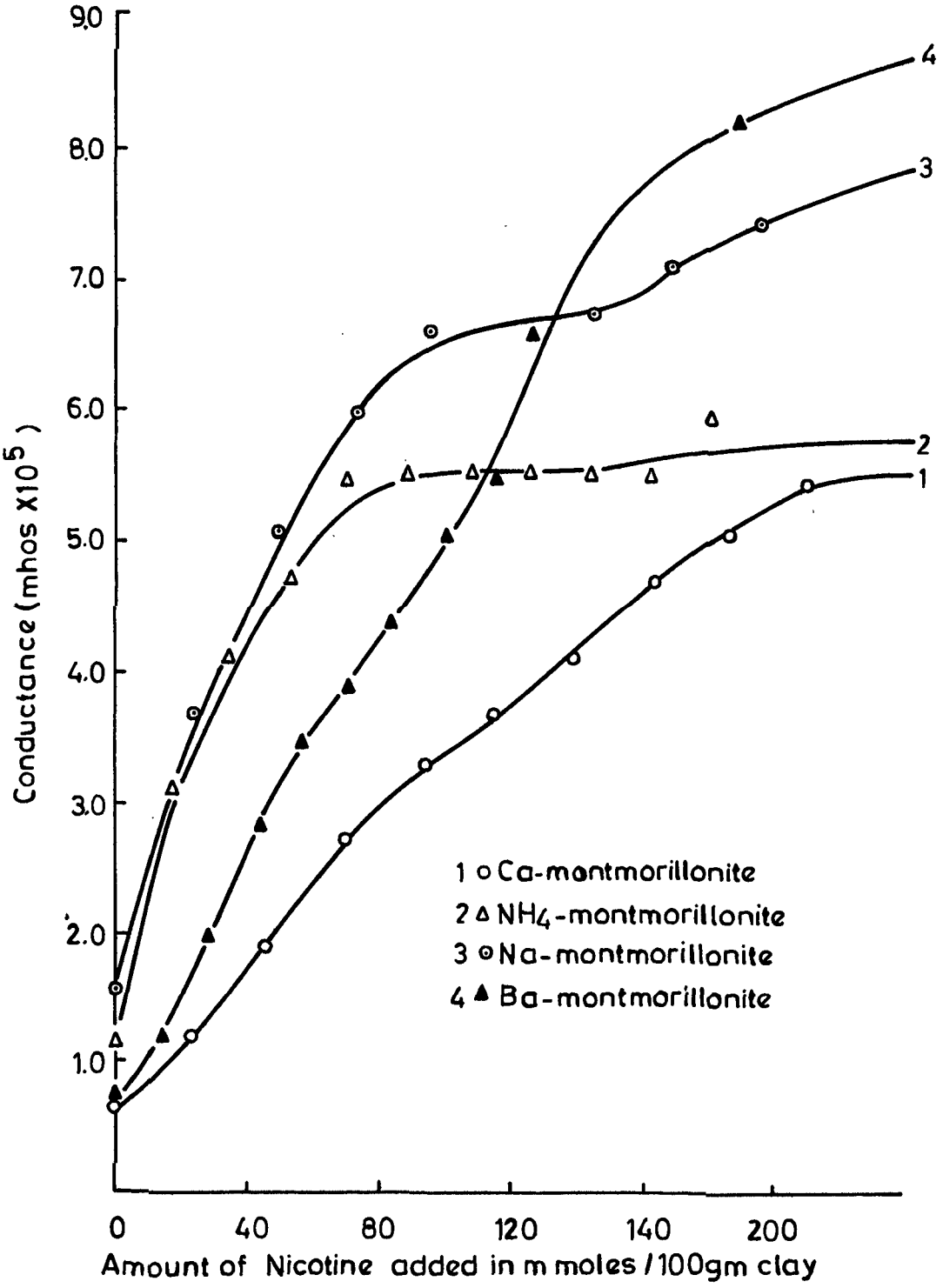


Fig. 7 Conductometric titrations of base saturated montmorillonite

Table XLV

Potentiometric and conductometric titrations of calcium montmorillonite with nicotine

Concentration of clay = 0.0530 gms/5ml suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = 0.03 N

Volume of nicotine in cc	Volume of water added in cc	Meq of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.00	7.00	0.73
0.4	19.6	23.25	7.30	1.17
0.8	19.2	46.50	8.00	1.93
1.2	18.8	69.75	8.25	2.74
1.6	18.4	93.00	8.35	3.25
2.0	18.0	116.25	8.45	3.65
2.4	17.6	139.50	8.55	4.11
2.8	17.2	162.75	8.65	4.69
3.2	16.8	186.00	8.70	5.06
3.6	16.4	209.25	8.80	5.48
4.0	16.0	233.50	8.95	5.48
5.0	15.0	290.69	9.15	5.48
6.0	14.0	348.03	9.25	5.48
7.0	13.0	406.90	9.30	5.48
8.0	12.0	467.00	9.30	5.48
9.0	11.0	529.06	9.30	5.48
10.0	10.0	581.38	9.30	5.48

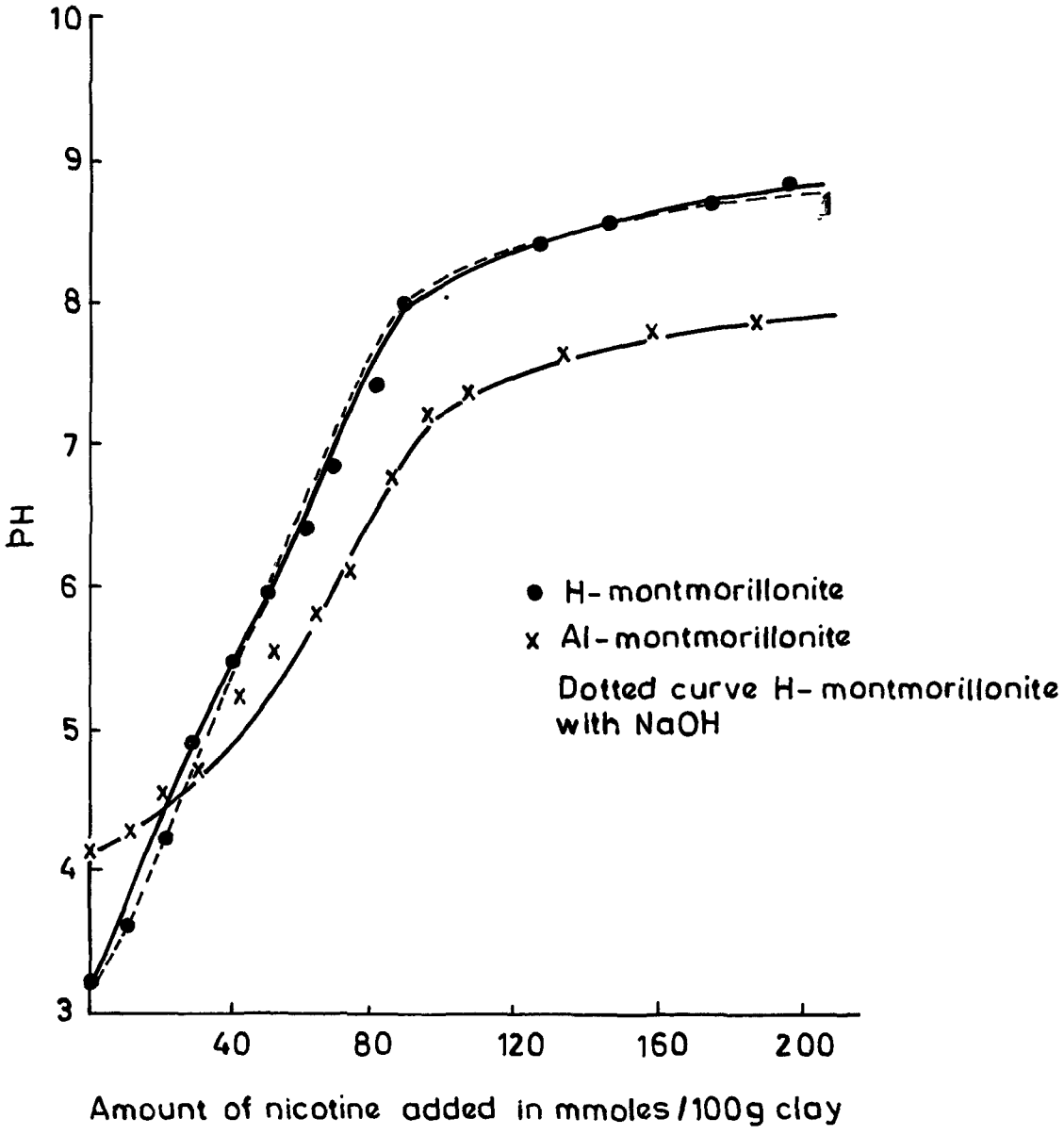


FIG. 8 PH titrations of hydrogen and base saturated montmorillonite with nicotine

Table XLVI

Potentiometric and conductometric titration of ammonium montmorillonite with nicotine

Concentration of clay = 0.0680 gms/5 ml suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = 0.03 N

Volume of nicotine in cc	Volume of water added in cc	Meq of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.00	6.25	1.19
0.4	19.6	18.09	6.40	3.13
0.8	19.2	36.18	6.80	4.11
1.2	18.8	54.27	7.30	4.69
1.6	18.4	72.36	7.70	5.48
2.0	18.0	90.45	8.00	5.48
2.4	17.6	108.54	8.20	5.48
2.8	17.2	126.63	8.30	5.48
3.2	16.8	144.72	8.40	5.48
3.6	16.4	162.81	8.50	5.48
4.0	16.0	180.90	8.60	5.98
5.0	15.0	226.24	8.60	5.98
6.0	14.0	271.04	8.60	5.98
7.0	13.0	316.74	8.70	6.57
8.0	12.0	361.80	8.75	6.57
9.0	11.0	407.23	8.85	6.57
10.0	10.0	452.48	8.85	6.57

Table XLVII

Potentiometric and conductometric titrations of sodium montmorillonite with nicotine

Concentration of clay = 0.0508 gms/5 cc suspension
Volume of clay suspension taken in different tubes = 5.0 cc
Strength of nicotine = 0.03 N

Volume of nicotine in cc	Volume of water added in cc	Meq of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.00	5.8	1.60
0.4	19.6	24.24	6.0	3.65
0.8	19.2	48.48	6.8	5.06
1.2	18.8	72.72	8.0	5.98
1.6	18.4	96.96	8.2	6.57
2.0	18.0	121.20	8.5	7.51
2.4	17.6	145.44	8.6	6.70
2.8	17.2	169.68	8.8	7.10
3.2	16.8	193.92	8.9	7.40
3.6	16.4	218.16	9.0	7.60
4.0	16.0	242.40	9.1	7.80
5.0	15.0	303.03	9.2	8.00
6.0	14.0	365.63	9.3	8.22
7.0	13.0	424.24	9.4	8.30
8.0	12.0	484.80	9.4	8.50
9.0	11.0	545.45	9.4	8.50
10.0	10.0	606.06	9.5	8.50

Table XLVIII

Potentiometric and conductometric titrations of barium montmorillonite with nicotine

Concentration of clay = 0.0844 gms/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = 0.03 N

Volume of nicotine in cc	Volume of water added in cc	Meq of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^{-4} mhos
0.0	20.0	0.00	6.00	0.75
0.4	19.6	14.35	8.00	1.19
0.8	19.2	28.70	8.10	1.99
1.2	18.8	43.05	8.25	2.86
1.6	18.4	57.40	8.45	3.47
2.0	18.0	71.75	8.70	3.86
2.4	17.6	86.10	8.65	4.38
2.8	17.2	100.45	8.65	5.06
3.2	16.8	114.80	8.65	5.48
3.6	16.4	129.15	8.70	6.56
4.0	16.0	143.50	8.65	8.22
5.0	15.0	179.85	8.80	8.22
6.0	14.0	215.82	8.85	8.50
7.0	13.0	249.20	8.85	8.80
8.0	12.0	287.00	8.85	8.80
9.0	11.0	323.73	8.70	8.80
10.0	10.0	359.70	8.70	8.80

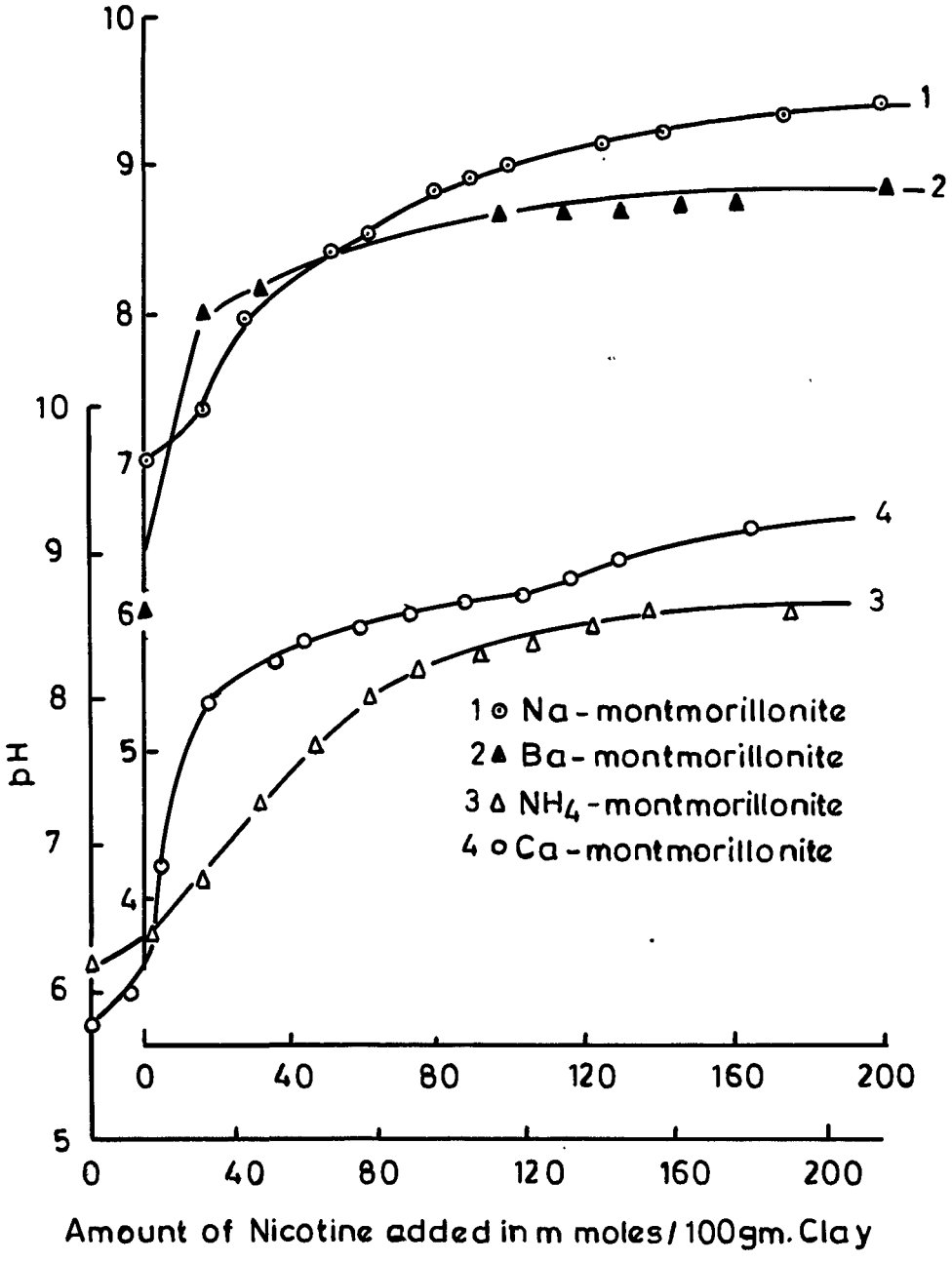


Fig. 9 PH titrations of base saturated montmorillonite

Set 2.

ADSORPTION OF NICOTINE BY MONTMORILLONITE

The adsorption experiments were carried out by taking 5.0 ml of the acids and base saturated montmorillonite suspensions in each case in a number of glass stoppered centrifuge tubes and adding varying concentrations of the standard nicotine solution (0.03%) and adjusting the mixture to a constant volume with distilled water. The tubes were fitted on a shaker and shaken for three hours each day for three days at a constant temperature to attain equilibrium. The mixtures were then allowed to sediment overnight, the supernatant liquids taken out, centrifuged and titrated with standard hydrochloric acid using methyl red as indicator to estimate the residual nicotine. The adsorption of nicotine was obtained from the change in concentration of the solution before and after contact with the clay. Curves were plotted between equilibrium concentration of nicotine and mmoles of nicotine adsorbed per 100g of clay. The results are given in tables XLIX (a) to LIV (a) and represented vide Figure 10, curves 1 to 6.

DETERMINATION OF Kd (ADSORPTION)

The Kd (molecular)[11] of nicotine in montmorillonite

suspensions was calculated from the relation

$$Kd = \frac{\text{Amount of nicotine per dry gram of clay after equilibrium}}{\text{Amount of nicotine per ml of liquid after equilibrium}}$$

$$= \frac{F - I}{I} \times \frac{\text{Total volume of the suspension}}{\text{Weight of the clay in the suspension}}$$

where F was the volume of nicotine added in ml and I was the volume of nicotine in equilibrium suspension. The results are given in tables XLIX (b) to LIV (b) and represented vide figures 11 and 12.

CALCULATION OF CORRELATION COEFFICIENTS

Correlation coefficients between amount of nicotine adsorbed and pH were calculated as per statistical methods of analysis and given in tables XLIX (b) to LIV (b).

Set 2.

Table XLIX (a)

Adsorption of nicotine by hydrogen saturated montmorillonite

(i)	Concentration of hydrogen saturated clay suspension	= 0.0662 gms/5 ml
(ii)	Weight of nicotine	= 0.50 gms/100 ml
(iii)	Strength of nicotine solution	= Strength of HCl soln.
(iv)	Indicator used	= Methyl red
(v)	Volume of suspension taken	= 5.0 ml
(vi)	Total volume of the mixture made upto	= 16.0 ml

Volume of nicotine soln. added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m moles/gm clay
0.00	0.00	0.000	0.00	0.000
0.40	0.00	0.000	0.40	0.186
0.80	0.00	0.000	0.80	0.372
1.20	0.00	0.000	1.20	0.558
1.60	0.08	0.154	1.52	0.707
2.00	0.16	0.308	1.84	0.856
2.40	0.48	0.924	1.92	0.893
2.80	0.80	1.540	2.00	0.931
3.20	1.04	2.003	2.16	1.005
3.60	1.44	2.863	2.26	1.005
4.00	1.76	3.389	2.24	1.042
5.00	2.56	4.930	2.44	1.135
6.00	3.52	6.779	2.48	1.154
7.00	4.48	8.628	2.52	1.173
8.00	5.44	10.477	2.56	1.191
9.00	6.40	12.326	2.60	1.210
10.00	7.20	14.167	2.80	1.303

Table XLIX (b)

Continuation of table XLIX (a)

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		3.20
100.00	∞		3.60
100.00	∞		4.30
100.00	∞		4.90
95.04	4590.00		5.50
92.00	2784.00		6.00
80.20	967.00		6.40
71.70	604.00		6.90
55.29	502.00	r = -0.506	7.40
49.35	362.00		8.00
46.83	306.80		8.10
48.70	230.50		8.40
41.40	170.30		8.60
36.10	135.90		8.70
32.00	117.00		8.80
28.90	98.35		8.80
28.00	94.00		8.80

Table L (a)

Adsorption of nicotine by aluminium saturated montmorillonite

(i) Concentration of aluminium clay suspension = 0.0622 gms/5 ml
(ii) Weight of nicotine = 0.50 gms/100 ml
(iii) Strength of nicotine soln. = Strength of HCl soln.
(iv) Indicator used = Methyl red
(v) Volume of suspension taken = 5.0 ml
(vi) Total volume of the mixture made upto = 16.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m moles/gm clay
0.0	0.00	0.000	0.00	0.000
0.4	0.00	0.000	0.40	0.198
0.8	0.00	0.000	0.80	0.396
1.2	0.00	0.000	1.20	0.594
1.6	0.08	0.154	1.52	0.742
2.0	0.32	0.616	1.68	0.831
2.4	0.64	1.232	1.76	0.871
2.8	0.96	1.848	1.84	0.914
3.2	1.24	2.388	1.96	0.970
3.6	1.59	3.062	2.01	0.995
4.0	2.16	4.160	1.84	0.910
5.0	2.80	5.392	2.20	1.089
6.0	3.92	7.549	2.08	1.029
7.0	4.00	7.704	3.00	1.485
8.0	5.68	10.939	2.32	1.148
9.0	6.80	13.096	2.20	1.089
10.0	7.60	14.637	2.40	1.118

Table L (b)

Continuation of table L (a)

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		4.10
100.00	∞		4.20
100.00	∞		4.50
100.00	∞		4.70
95.00	782.00		5.25
84.00	135.00		5.50
73.40	70.60		5.75
65.70	49.35		6.05
61.30	40.60	r = -0.594	6.70
55.00	32.50		7.25
46.00	21.98		7.30
44.10	20.10		7.60
34.70	13.69		7.75
42.00	19.25		7.80
29.00	10.50		7.95
24.45	8.34		8.10
24.00	8.14		8.20

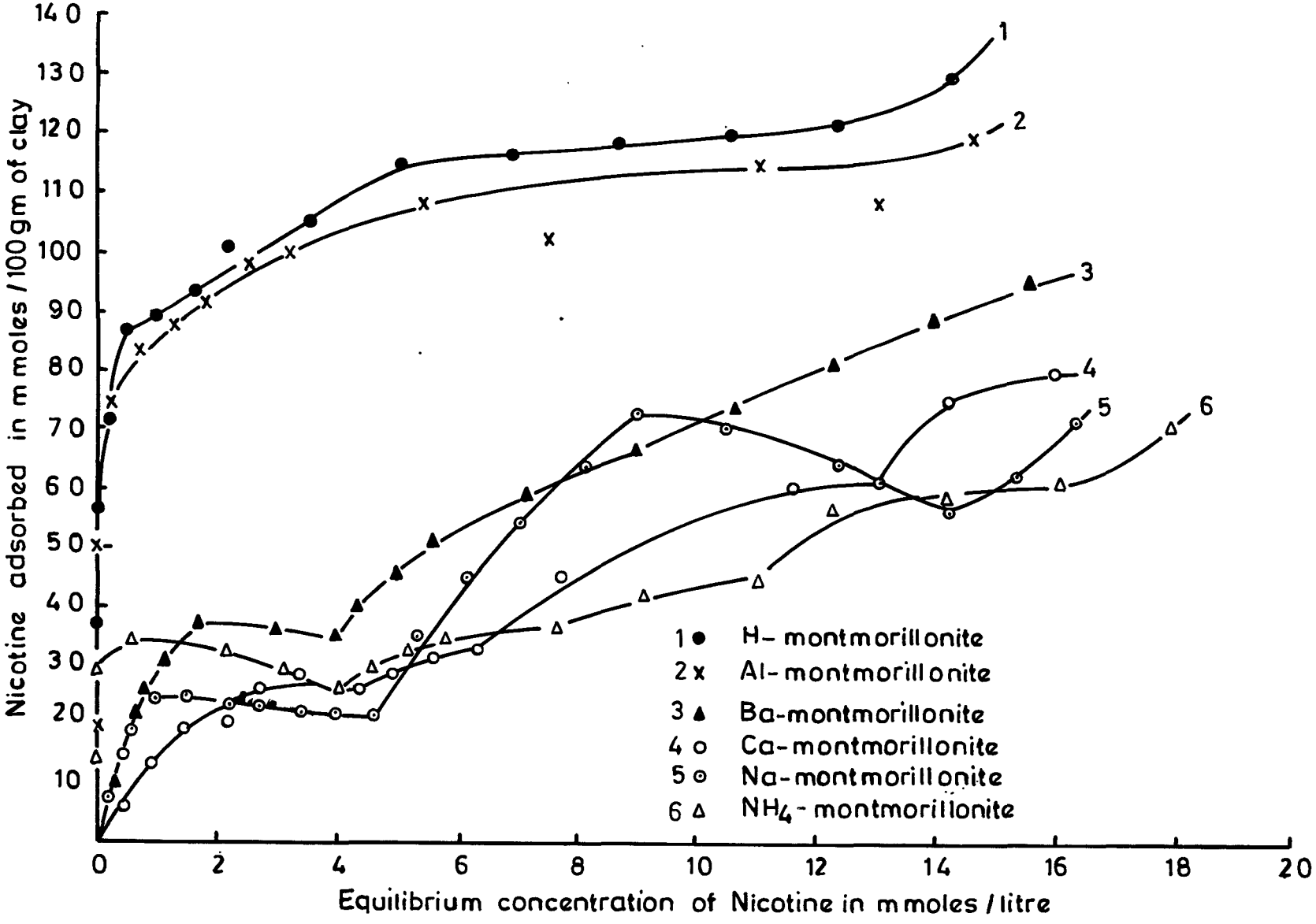


Fig. 10 Adsorption isotherms for the adsorption of Nicotine by hydrogen and base saturated Montmorillonites

Table LI (a)

Adsorption of nicotine by barium montmorillonite

(i) Concentration of sodium clay suspension = 0.0774 gms/5 ml

(ii) Weight of nicotine = 0.50 gms/100 ml

(iii) Strength of nicotine soln. = Strength of HCl soln.

(iv) Indicator used = Methyl red

(v) Volume of the suspension taken = 5.0 ml

(vi) Total volume of the mixture made upto = 15.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m moles/gm clay
0.00	0.000	0.000	0.000	0.000
0.40	0.136	0.278	0.264	0.105
0.80	0.272	0.556	0.524	0.210
1.20	0.543	0.834	0.657	0.261
1.60	0.815	1.112	0.784	0.313
2.00	1.086	1.668	0.914	0.364
2.40	1.493	2.976	0.907	0.361
2.80	1.901	3.903	0.899	0.358
3.20	2.172	4.257	1.028	0.410
3.60	2.444	5.021	1.156	0.460
4.00	2.715	5.594	1.285	0.511
5.00	3.530	7.250	1.470	0.585
6.00	4.340	8.924	1.656	0.659
7.00	5.159	10.597	1.841	0.733
8.00	5.973	12.271	2.027	0.807
9.00	6.786	13.944	2.214	0.881
10.00	7.602	15.619	2.394	0.954

Table LI (b)

Continuation of table LI (a)

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		6.00
377.00	65.00		8.00
377.00	66.30		8.10
234.00	55.00		8.25
186.50	49.40		8.45
163.20	45.50		8.70
117.85	37.90		8.65
91.55	32.20		8.65
91.80	32.20		8.65
91.80	32.20	r = -0.440	8.70
91.80	31.95		8.65
80.90	29.40		8.60
73.90	27.65		8.65
69.75	26.20		8.85
65.85	25.25		8.85
63.40	24.55		8.70
61.00	24.00		8.70

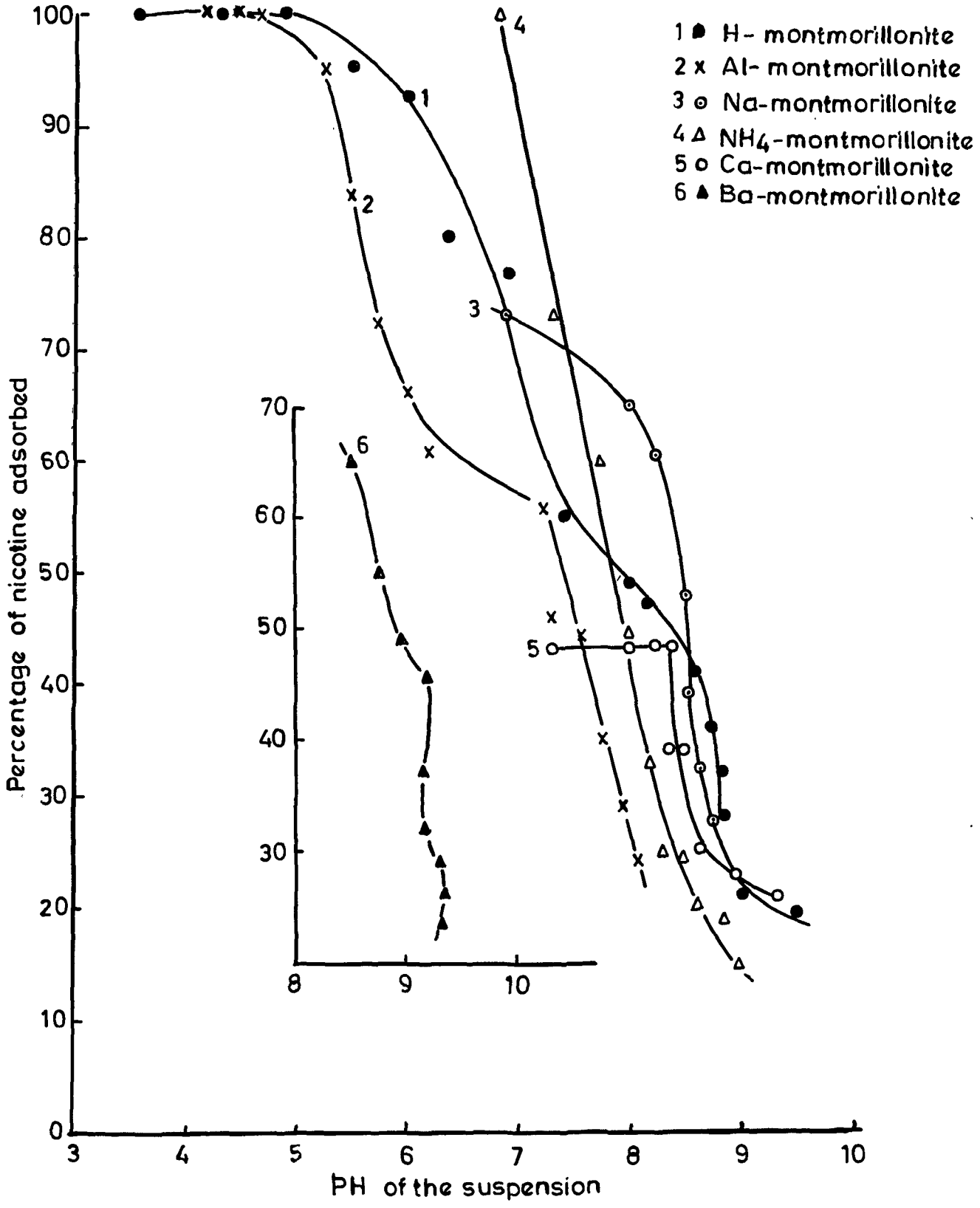


Fig. 11 Effect of PH on the adsorption of nicotine by hydrogen and base saturated montmorillonite

Table LII (a)

Adsorption of nicotine by calcium montmorillonite

(i) Concentration of calcium clay suspension = 0.0856 gm/5 ml

(ii) Weight of nicotine = 0.50 mg/100 ml

(iii) Strength of nicotine solution = Strength of HCl soln.

(iv) Indicator used = Methyl red

(v) Volume of the suspension taken = 5.0 ml

(vi) Total volume of the mixture made upto = 15.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m moles/gm clay
0.0	0.000	0.000	0.000	0.000
0.4	0.225	0.463	0.175	0.063
0.8	0.450	0.926	0.350	0.126
1.2	0.675	1.389	0.525	0.189
1.6	1.050	2.150	0.550	0.198
2.0	1.325	2.720	0.675	0.243
2.4	1.625	3.330	0.775	0.279
2.8	2.100	4.310	0.700	0.252
3.2	2.400	4.920	0.800	0.288
3.6	2.700	5.540	0.900	0.324
4.0	3.075	6.310	0.925	0.333
5.0	3.750	7.700	1.250	0.450
6.0	-	-	-	-
7.0	5.625	11.550	1.375	0.495
8.0	6.300	12.940	1.700	0.612
9.0	6.900	14.180	2.100	0.756
10.0	7.800	16.020	2.200	0.792

Table LII (b)

Continuation of table LII (a)

Percentage of nicotine absorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		7.00
43.70	136.82		7.30
43.70	136.82		8.00
43.70	136.82		8.25
34.30	91.76		8.35
33.80	89.40		8.45
31.90	83.60		8.55
25.00	58.50		8.65
24.30	58.50		8.70
25.20	58.40	r = -1.380	8.80
23.20	52.70		8.95
25.00	58.50		9.15
-	-		-
19.65	42.80		9.30
21.20	47.35		9.30
23.35	53.33		9.30
21.75	49.46		9.30

Table LIII (a)

Adsorption of nicotine by sodium montmorillonite

(i) Concentration of sodium clay suspension = 0.1246 gms/5 ml
(ii) Weight of nicotine = 0.50 gms/100 ml
(iii) Strength of nicotine soln. = Strength of HCl soln.
(iv) Indicator used = Methyl red
(v) Volume of suspension taken = 5.0 ml
(vi) Total volume of the mixture made upto = 21.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m mhos/gm clay
0.00	0.000	0.000	0.000	0.000
0.40	0.105	0.154	0.295	0.073
0.80	0.210	0.303	0.590	0.146
1.20	0.420	0.616	0.780	0.193
1.60	0.630	0.924	0.970	0.240
2.00	1.050	1.540	0.950	0.235
2.40	1.470	2.150	0.930	0.230
2.80	1.890	2.770	0.910	0.225
3.20	2.310	3.380	0.890	0.220
3.60	2.730	4.000	0.870	0.215
4.00	3.150	4.620	0.850	0.210
5.00	3.570	5.280	1.430	0.353
6.00	4.200	6.160	1.800	0.445
7.00	4.830	7.080	2.170	0.536
8.00	5.460	8.010	2.540	0.627
9.00	6.090	8.930	2.910	0.719
10.00	7.140	10.470	2.860	0.706
11.00	8.400	12.320	2.600	0.642
12.00	9.660	14.170	2.340	0.578
13.00	10.500	15.400	2.500	0.618
14.00	11.130	16.330	2.870	0.709

Table LIII (b)

Continuation of table LIII (a)

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		5.80
73.60	473.50		6.00
73.60	473.50		6.80
65.00	313.00		8.00
60.70	259.00		8.20
47.60	153.46		8.50
38.80	106.72		8.50
32.50	79.62		8.60
27.80	64.45		8.80
24.20	53.73	r = -0.454	8.90
21.30	45.76		9.00
20.65	67.48		9.10
30.00	72.69		9.20
31.00	75.69		9.30
31.70	78.44		9.40
32.40	80.40		9.40
28.60	67.48		9.40
23.40	50.00		9.50
19.45	40.95		9.50
19.25	40.76		9.50
20.50	43.36		9.50

Table XIV (a)

Adsorption of nicotine by ammonium montmorillonite

(i) Concentration of ammonium clay suspension = 0.0810 gms/5 ml
(ii) Weight of nicotine = 0.50 gms/100 ml
(iii) Strength of nicotine soln. = Strength of HCl soln.
(iv) Indicator used = Methyl red
(v) Volume of suspension taken = 5.0 ml
(vi) Total volume of the mixture made upto = 16.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in m moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in moles/gm clay
0.00	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.400	0.143
0.80	0.000	0.000	0.800	0.296
1.20	0.320	0.616	0.980	0.351
1.60	0.640	1.232	0.960	0.343
2.00	1.120	2.157	0.900	0.325
2.40	1.600	3.080	0.800	0.296
2.80	2.080	4.062	0.720	0.257
3.20	2.400	4.620	0.800	0.296
3.60	2.720	5.239	0.880	0.325
4.00	3.040	5.855	0.960	0.343
5.00	4.000	7.700	1.000	0.357
6.00	4.800	9.240	1.200	0.428
7.00	5.760	11.090	1.240	0.443
8.00	6.400	12.320	1.600	0.571
9.00	7.360	14.170	1.640	0.585
10.00	8.320	16.020	1.680	0.601

Table LIV (b)

Continuation of table LIV (a)

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		6.25
100.00	∞		6.40
100.00	∞		6.80
73.40	605.00		7.30
60.00	296.40		7.70
44.00	155.00		8.00
33.40	98.80		8.20
24.80	68.48	r = -0.270	8.30
25.00	65.80		8.40
24.40	63.85		8.50
23.95	62.40		8.60
20.00	49.45		8.60
20.00	49.45		8.60
17.70	43.15		8.70
20.00	49.45		8.75
18.20	44.00		8.85
16.77	40.00		8.85

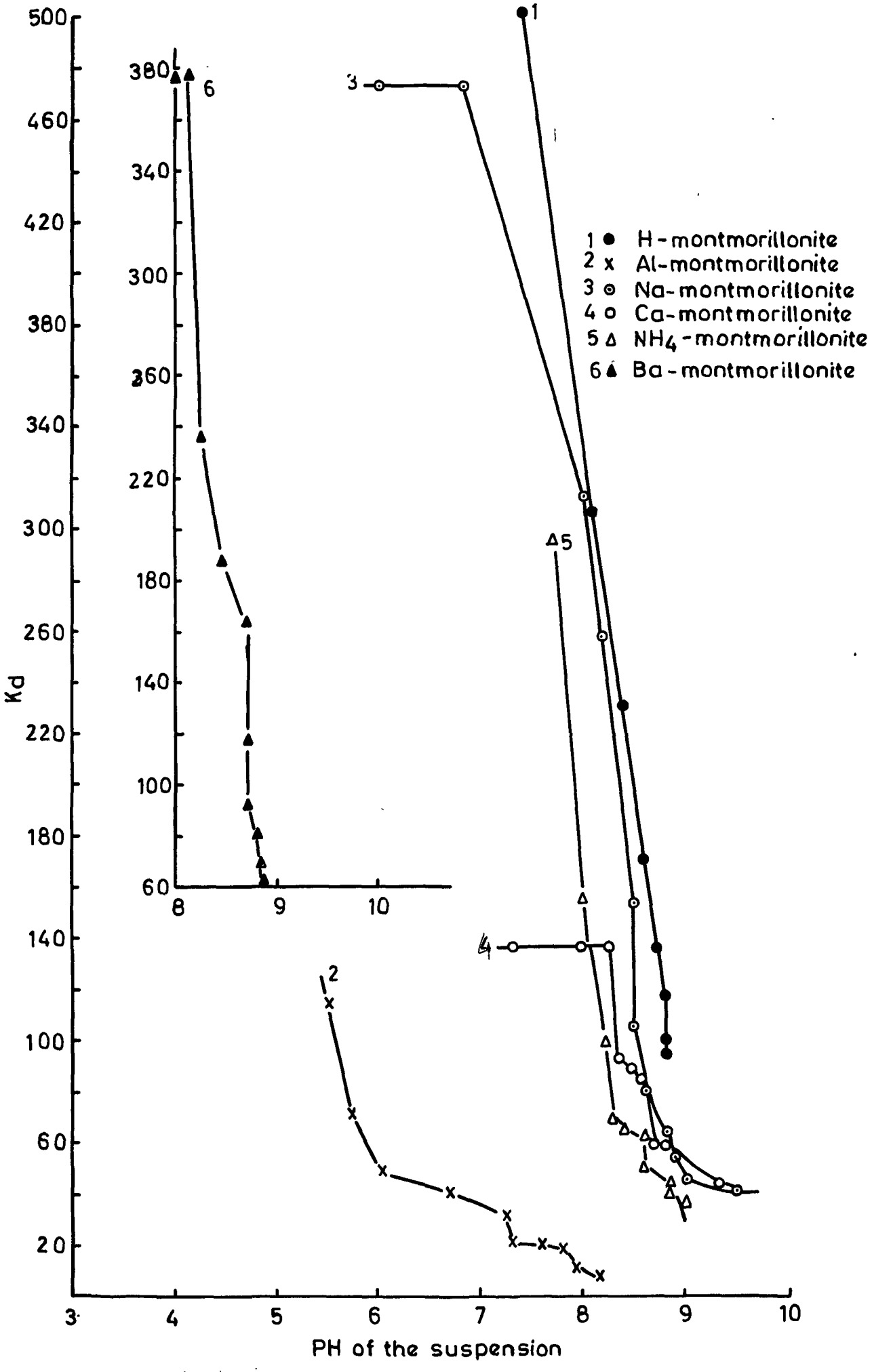


Fig. 12 Variation in distribution coefficient (molecular) with PH of the montmorillonite suspensions

Set 3.

Desorption of nicotine from nicotinium clays

Desorption of nicotine was done by washing the nicotinium clay with distilled water. During the experiments it was, however, noticed that the amount of base in the desorbed liquid was greater in case of ammonium, sodium, barium and calcium montmorillonites than the amount of nicotine added during adsorption experiments (vide tables LV to LVIII). Hence the quantitative measurements of the desorbed nicotine could not be done by HCl titration. Other methods too did not yield satisfactory results. To trace the origin of the excess base, the cationic concentration viz., Na^{+}, Ba^{++} and Ca^{++} in the supernatant liquid of the sodium, barium, and calcium montmorillonites before and after addition of nicotine, was determined by flame photometer, O-Cresolphthalein complexone method and versenate titration respectively. The results are given in table LIX.

Set 3.

Table LV

Effect of water treatment on nicotinium clay complex of ammonium montmorillonite

Concentration of clay = 0.0310 gm/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = Strength of HCl = 0.03N

Amount of nicotine added in m moles/100 gm clay	HCl used in back titration in cc on the filtered complex	Base decorbed on water treatment in m moles/100 gm	Excess base decorbed in m moles/100 clay
0.00	0.00	0.00	0.00
15.20	2.00	76.04	60.84
30.40	5.00	114.06	83.66
45.60	5.40	129.27	83.67
60.80	5.40	129.27	68.47
76.00	5.40	129.27	53.23

Table LVI

Effect of water treatment on nicotinium clay complexes of sodium montmorillonite

Concentration of clay = 0.1246 gm/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = Strength of HCl = 0.03N

Amount of nicotine added in m moles/100 gm clay	HCl used in back titration in cc of the filtered complex	Base desorbed on water treatment in m moles/100 gm clay	Excess base desorbed in m moles/100 gm clay
0.00	0.00	0.00	0.00
9.92	0.40	9.92	0.00
19.84	0.80	19.84	0.00
29.76	1.20	29.76	0.00
39.68	1.60	39.68	0.00
49.60	2.00	49.60	0.00

Table LVII

Effect of water treatment on nicotine-montmorillonite complex of barium montmorillonite

Concentration of clay = 0.0774 gm/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0

Strength of nicotine = Strength of HCl = 0.03N

Amount of nicotine added in m moles/100 gm clay	HCl used in back titration in m moles of the filtered complex	Base desorbed on water treatment in m moles/100 gm clay	Excess base adsorbed in m moles/ 100 gm clay
0.00	0.00	0.00	0.00
15.94	1.20	47.61	32.13
31.87	1.40	55.78	23.91
47.81	1.80	63.74	15.93
63.74	1.88	71.71	7.93
79.68	2.00	79.68	0.00

Table XVIII

Effect of water treatment on nicotinium clay complexes of calcium montmorillonite.

Concentration of clay = 0.0856 gms/5 cc suspension

Volume of clay suspension taken in different tubes = 5.0 cc

Strength of nicotine = Strength of HCl = 0.03N

Amount of nicotine added in m moles/100gm clay	HCl used in back titration in m moles of the filtered complex	Base desorbed on water treatment in m moles/100gm clay	Excess base desorbed in m moles/ 100 gm clay
0.00	0.00	0.00	0.00
14.33	0.60	21.70	7.32
28.76	1.40	50.36	21.60
43.14	1.00	64.75	21.61
57.52	2.20	79.13	21.61
71.90	2.60	93.52	21.62

Table LIX

Increase in cationic concentration in m moles/100 gm clay in the equilibrium liquid of clays on addition of nicotine.

Cation	Concentration before nicotine treatment	Concentration after nicotine treatment	Increase expressed as hydroxide
Na^{+}	11.07	22.14	11.07
Ba^{++}	11.90	32.40	14.50
Ca^{++}	21.31	42.62	21.31

Set 4.

X-RAY ANALYSIS

X-ray analysis was carried out on sodium-saturated samples of montmorillonite, and nicotine treated montmorillonites. The nicotine treatment was done upto and three additional concentrations beyond the DLC. For X-ray examination the samples were oriented on glass microslides from a water suspension at room temperature. Patterns were recorded after air drying and after heat treatment of the samples at 550 C for two hours using filtered Cu Kα radiation on a Philips diffraction unit and Hiercmete goniometer at a speed of 2 degrees per minute.

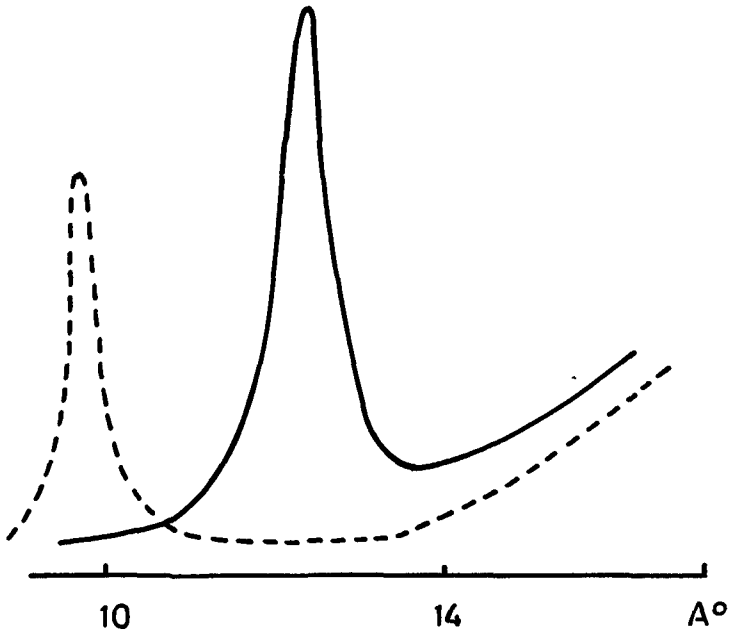
The X-ray patterns were interpreted on the following basis:

1. X-ray diffraction spacings obtained from (001) planes of layer silicate species related to sample treatment.
2. The intensities of diffraction maxima by measuring of d - spacing peak heights.
3. The intensities of diffraction maxima by measuring of the areas under d - spacing peaks. The results are recorded in table LX, figure 13.

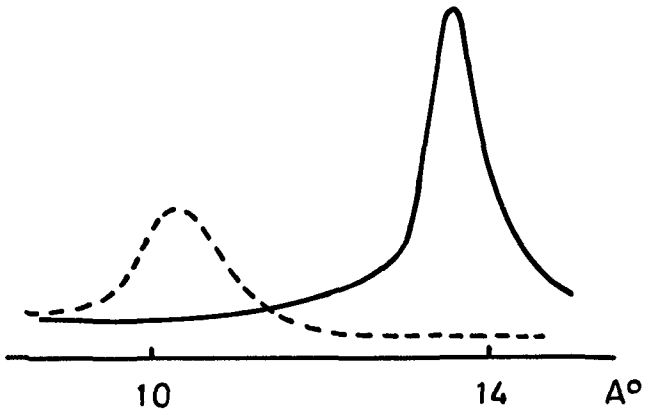
Table LX

Basal spacings of sodium saturated and nicotine treated montmorillonites

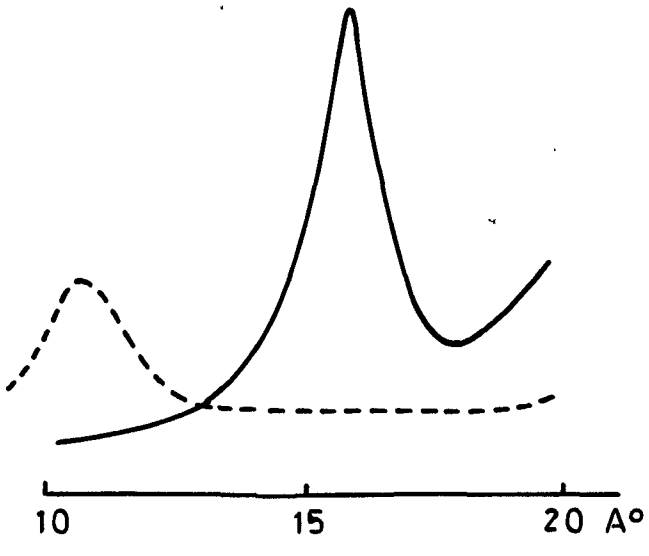
Cation and its conc. in m moles/100gm clay	Basal spacings, Å	
	air dried	heated at 550°C
Sodium (90)	11.9 - 12.2	9.4
Nicotine (90)	13.55	10.5
Nicotine (150)	15.03	10.5
Nicotine (250)	15.22	10.5
Nicotine (450)	15.22	10.5



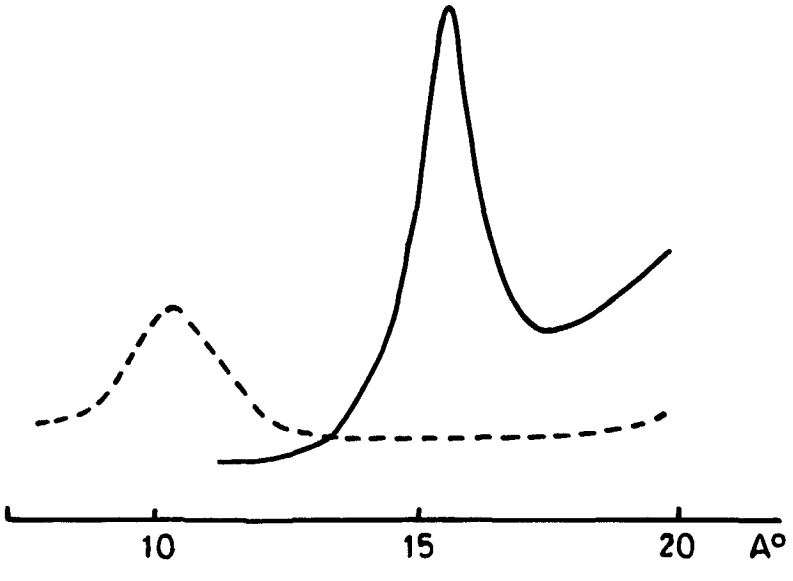
Sodium montmorillonite



Nicotinium montmorillonite
(Nicotine treatment upto BEC)



Nicotinium montmorillonite
Nicotine treatment upto 150 m moles 100 gm clay)



Nicotinium montmorillonite
(Nicotine treatment upto 450
m moles /100 gm clay)

Fig. 13 X-ray diffractograms of sodium and nicotine saturated montmorillonites

Set 5.

Differential Thermal Analysis

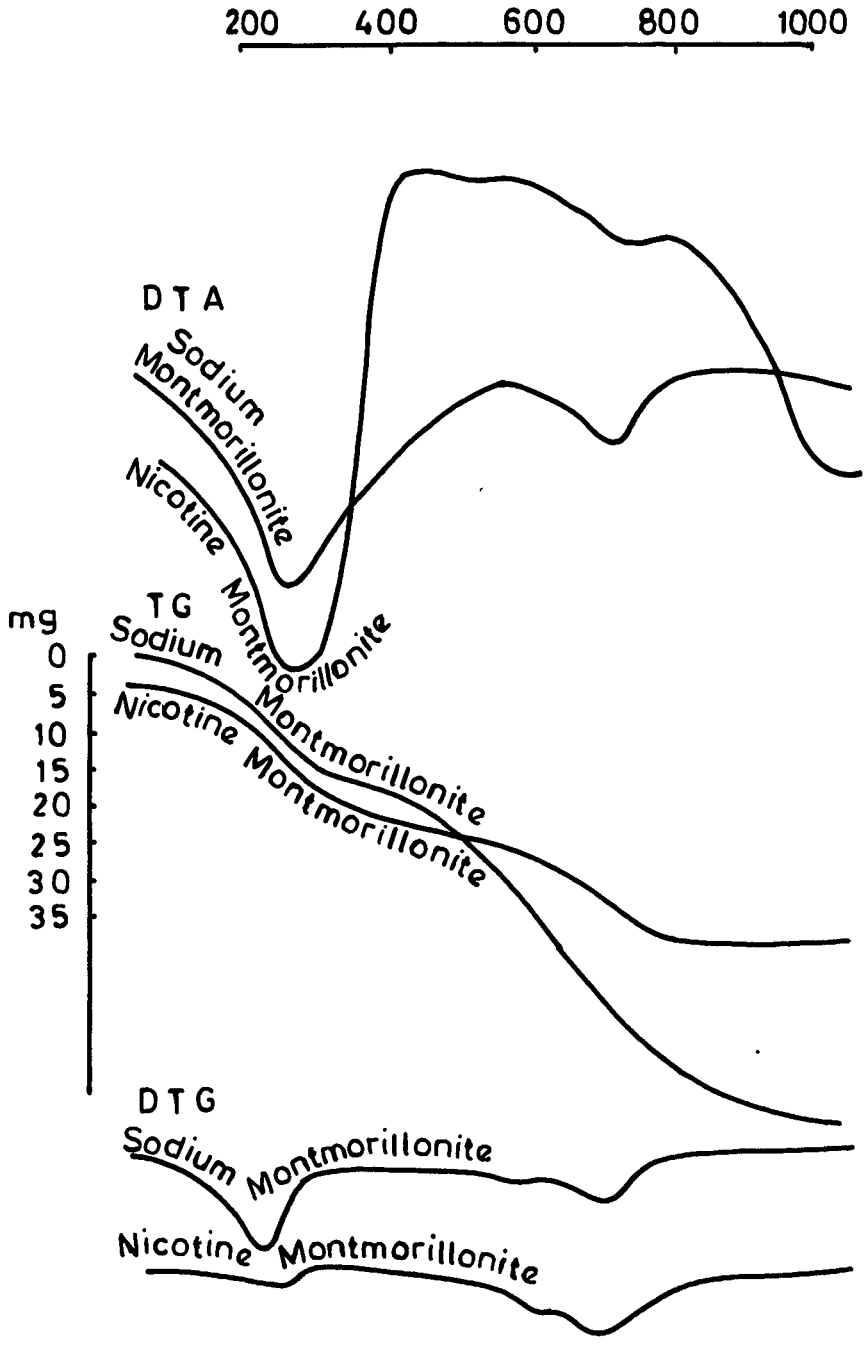
Differential Thermal Analysis were performed on a MOM Derivatograph Thermal Analyser, using platinum and platinum-rhodium thermocouples from room temperature to 1000°C at a constant rise of 20°C per minute. Ignited Al_2O_3 was used as inert reference substance. The samples were dried at 70°C for 3 hours before the analysis.

The quantity of the samples used for the thermal analysis were 300mg in both the cases. The DTA, TG and DTG curves were obtained in case of the same analysis. The results are represented vide figure 14 and loss in weight recorded in table LXI.

Table LXI

Percentage decrease in weight of montmorillonite samples

Samples	0-300°C	300-700°C	700-1000°C	Total summation
Aluminium montmorillonite	4.66	16.00	19.30	39.96
Sodium montmorillonite	5.66	12.30	12.30	32.26



FIG·14 DTA DTG, &TG CURVES FOR SODIUM & NICOTINIUM MONTMORILLONITES

Results and Discussion

To suitably characterise the hydrogen and base saturated montmorillonites, they were subjected to conductometric and potentiometric titrations with nicotine. The results are shown in Figures 6 to 9 respectively. Absence of multiple inflections in the titration curves confirmed the homoionic saturated nature of the clays prepared for the investigations. A sharp inflection at 90 m moles in the conductometric and potentiometric titrations of hydrogen clay with nicotine as well as with sodium hydroxide gave the B.C of clay as 90 meq/100g clay.

The results of adsorption of nicotine by the above suspensions (1.70 to 3.00% w/v) in the concentration range of 0 to 20 m moles of nicotine per litre are represented by isotherms (Figure 10, Curves 1 to 6). The curves exhibited discontinuities with maxima and minima at a few places. Such complexities in adsorption isotherms with occurrence of inflections and plateaus or dips, though not common, have been observed by several workers[12,13], in solute-solute-solvent systems and they underwent complete saturation. An examination of the isotherms given in Figure 10, Curves 1 to 6 showed a marked difference in the adsorption of nicotine by hydrogen and aluminium saturated montmorillonites as compared to that of the base saturation systems. The initial

parts of the isotherms of the acid saturated clays exhibited a characteristic vertical curves till about the base exchange capacity was reached. Here the nicotine seemed to have such a high affinity for the system that in dilute solution it was completely adsorbed. This continued up to a pH value of 5.0 with infinite values of Kd molecular (Table XXII). This process

Table XXII

Adsorption of nicotine by acid and base saturated montmorillonites at different equilibrium concentrations and the correlation coefficients between pH and adsorption.

Sample	pH	Equilibrium concentration in m.eq/litre	Amount adsorbed in m.eq/100g clay	Percentage adsorbed	Correlation Coefficient	Kd
H-clay	4.2	0.000	10.00	100.00		∞
	4.9	0.000	50.00	100.00		∞
	5.5	0.154	70.75	95.00	r = -0.966	500.00
	7.5	2.000	100.00	50.50		400.00
	8.5	4.000	101.00	44.00		100.00
	9.0	-	-	-		
Al-clay	4.2	0.000	10.00	100.00		∞
	4.7	0.000	50.40	100.00		∞
	5.5	0.016	72.16	94.00	r = -0.994	100.00
	7.5	5.700	99.98	44.50		20.00
	8.5	-	-	-		
	9.0	-	-	-		

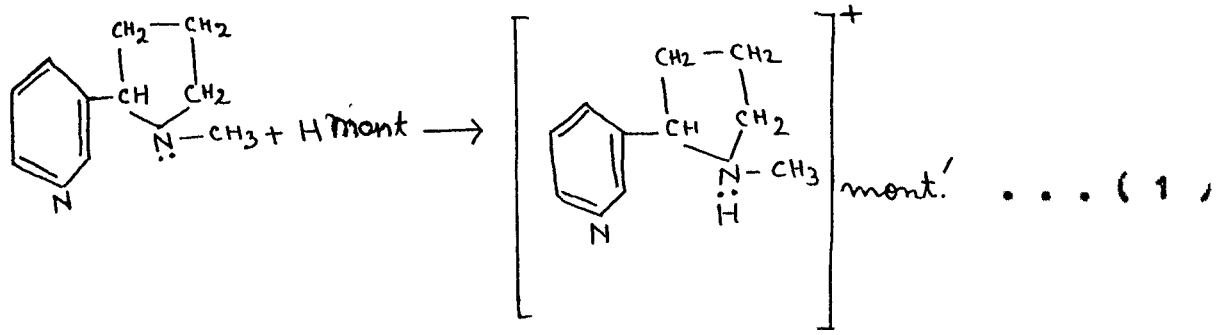
Table [illegible]

CONTINUED

Sample	pH	Equilibrium concentration in mg/litre	Amount adsorbed in mg/100g clay	Adsorption bed	Correlation coefficient	d
Ca-clay	4.2	-	-	-		-
	5.5	-	-	-		-
	7.5	0.600	10.50	69.50	r =-0.454	300.00
	8.5	0.900	22.50	39.00		107.00
	9.0	0.700	20.00	21.00		45.75
NH_4-clay	4.2	-	-	-		-
	5.5	-	-	-		-
	7.5	0.600	35.00	60.00	r =-0.370	530.00
	8.5	0.200	31.00	64.50		94.00
	9.0	10.700	60.00	15.00		30.00
Ca-clay	4.2	-	-	-		-
	5.5	-	-	-		-
	7.5	0.600	8.00	43.70	r =-1.330	150.00
	8.5	2.000	23.00	52.50		64.00
	9.0	6.300	35.00	22.50		52.00
Ba-clay	4.2	-	-	-		-
	5.5	-	-	-		-
	7.5	0.200	5.00	69.50	r =-0.440	377.00
	8.5	1.200	32.00	49.50		1[illegible].00
	9.0	-	-	-		-

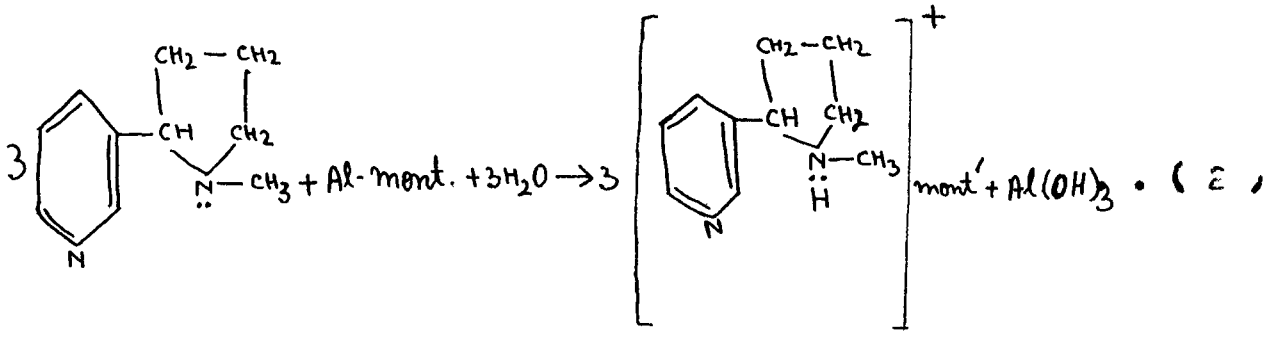
of cation adsorption at low pH appeared to be due to the protonation of the nicotine molecule by hydrogen ions, available either in the dimension or on the clay surface, followed by

adsorption of the nicotine cation on the lateral surface of montmorillonite. This reaction with hydrogen montmorillonite could be represented as



. . . (1)

the protonation occurring at the more basic pyrrolidine ring nitrogen of the nicotine molecule. That this adsorption occurred on the lateral surface found confirmation from x-ray data which showed an increase in basal spacing from 9.40Å to 13.35Å (Table Ia). The aluminium montmorillonite on the other hand, acting more or less as a bronsted acid[14] in dilute suspensions at a low pH, adsorbed nicotine according to the following equation:



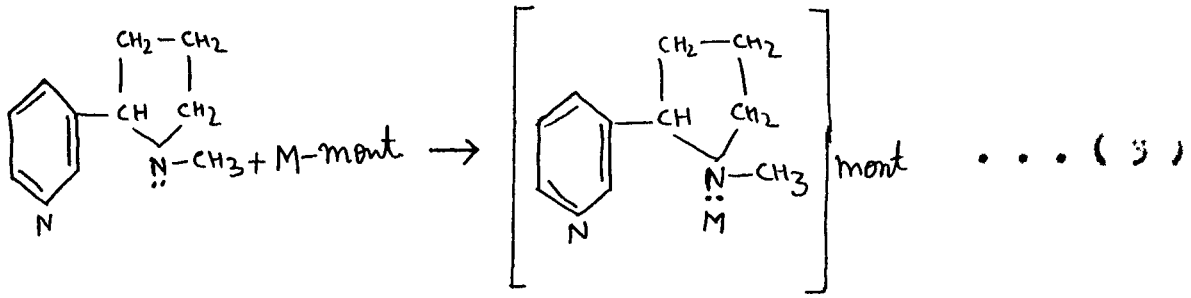
(2)

These propositions were found to be in accordance with the conductance and pH observations. That there was

formation of a nicotinium ion with lower mobility was accounted for by a decrease in conductance on the addition of nicotine to hydrogen montmorillonite. Similarly the increase in pH was due to elimination of protons from the exchangers (Figures 6 and 8, Curves 2 and 2). When all the protons had been removed as indicated by the above equations, the conductance and pH both became constant except for a minor rise in conductance associated with the nicotinium ion. At the above equivalents for initial high capacity of nicotine for acid clays not saturated, a point of slight decrease saturation occurred giving rise to an inflection in the adsorption isotherms.

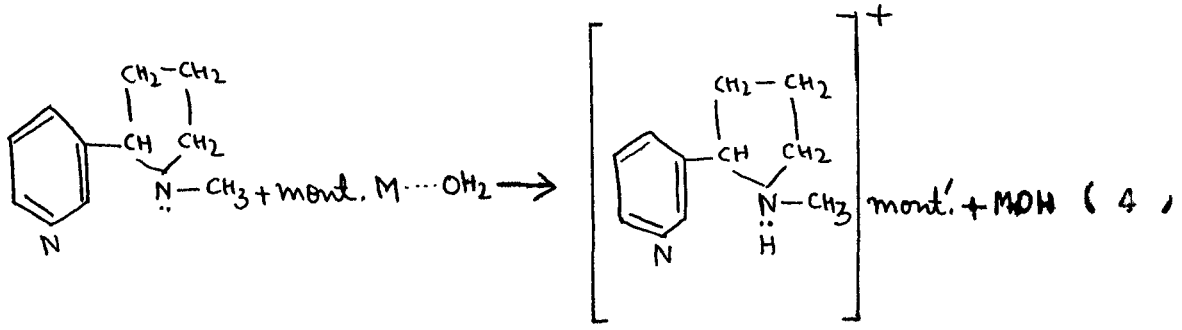
A high initial affinity of nicotine for the base saturated systems viz., ammonium, sodium, calcium and barium clays was also observed but the adsorption forces appeared to be weaker as that the inflection occurred at a much lower value. The adsorption at this point followed the order $H^+ > Al^{+++} > Ba^{++} > NH_4^+ > Na^+ > Ca^{++}$ (Figure 10). Reduced adsorption in base saturated systems appeared to be due to the relative availability of protons in base saturated montmorillonite at these pH values (7.5 and higher) and a reduction in acid character on base saturation. The results were in agreement with the observations of Hayes, Stacey and Thomas[15] on the adsorption of nicotine in humic acid. In analogy with the interactions[16] of some organic bases such as ethylamine and pyridine with exchange-

able cations in clays, it appeared, that the adsorption in these systems was partly due to formation of coordination bonds, such as,



. . . (3)

and partly due to the capacity of the nicotine to decomposition water from around the cations giving rise to protons by the formation of nicotinium ions and hydroxide in the interlayer space



(4)

The possibilities of such coordinations and proton transfer reactions in clays by these molecules were also suggested by several other workers[17,18,19,20]. That such reactions occurred found confirmation in these investigations. Thus, the increase in conductance observed on addition of nicotine to bentonite systems were in accordance with the coordi-

nating power of the exchangeable cations and the formation of basic hydroxides observed vide equation (3) and (4) respectively.

Evidence for the formation of hydroxides was also available from the formation of dips in the isotherms, as well as, from Table LXI which indicated an increase in the exchangeable cation content in the equilibrium liquid on addition of nicotine. The fact that the cation involved was present as a hydroxide was evident from the fact that the amount of base in the desorbed liquid was greater than the amount of nicotine added (vide Table LXIII)

Table LXIII

Effect of water treatment on nicotinium clay complexes in m moles/100g clay

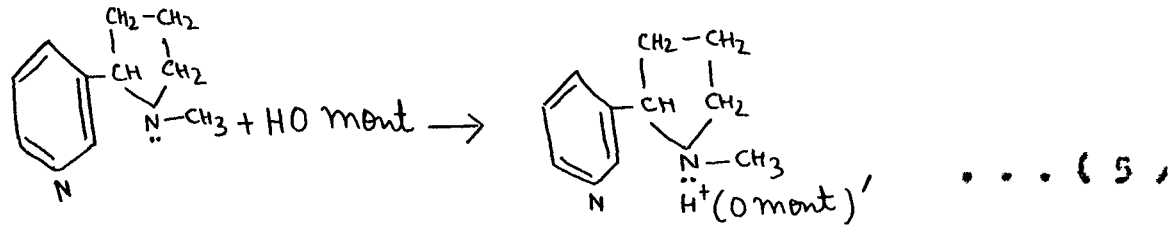
Clay form	Amount of nicotine added	Base desorbed on water treatment	Excess base desorbed
Na-clay	9.62	9.62	0.00
Ba-clay	16.06	48.19	32.13
Ca-clay	14.30	21.70	7.32
NH_4-clay	15.20	76.04	60.84

In all the cases considered above, as the initial adsorptive forces were saturated, an inflection occurred and

the curves changed their direction. Despite of all efforts to attain equilibrium, the discontinuities in the isotherms persisted. The curves were irreproducible except for small deviations of 2 to 4 m moles in the amount of nicotine adsorbed by the clay. The inflections followed by dips or plateaus[12] in some of the systems were a pointer that the first stage of saturation was being completed with the formation of a monolayer of nicotine ions on the most active sites of montmorillonite, which could or could not be closed packed. The layer probably contained water molecules as well and the small dips observed in this region probably resulted from a release of nicotinium ions either due to a competition between water and nicotine for adsorption on clay surface, or as a result of an increase in the attraction between nicotine and water at higher concentrations and pH, as compared to that between nicotine and the clay surface.[41]

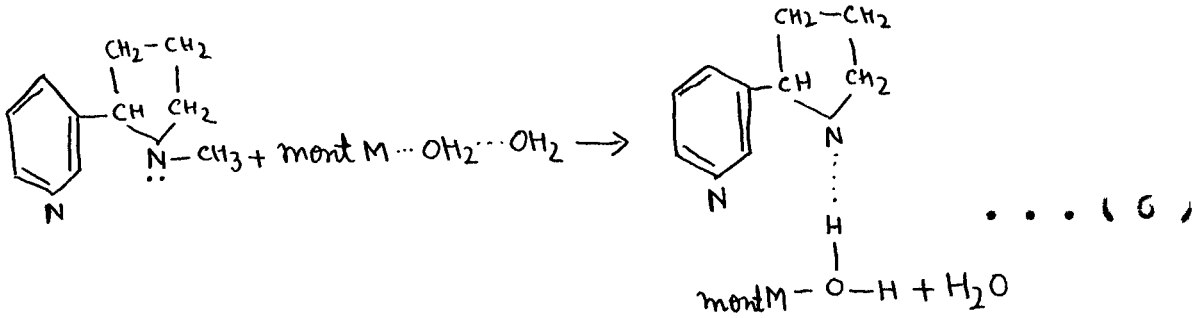
The subsequent rise in adsorption, which was quite substantial beyond the dips, was indicative of the formation of a fresh surface or surfaces on the clay layers after the high energy barrier for initial adsorption had been overcome by nicotine molecules. Three types of effects seemed to predominate in the higher concentration ranges., (i) a reorientation of the nicotine molecules from coplanar to upright configuration[23]; which ex post facto provided lateral surfaces for adsorption resulted in an increase in basal spacing from 13.55 to 15.4Å (Table 4a), (ii) build-

ding up of nicotine molecules on the outer surfaces of the clays followed by interaction with the weakly acidic hydroxyls[24] at the edges as follows



. . . (5)

and (iii) disruption[25] of sorbed water from around the mono and divalent cations and formation of hydrogen bonds with the directly coordinated water



. . . (6)

It had been suggested that when an organic molecule is strongly attached to the clay surface by chemical bonds, it is not lost to a sufficiently high temperature.[26] Due to structural differences[27] the nicotinium ions formed in the lattice layers vide equations 1, 2, 3 and 4 would not be accessible to oxidation as the ions formed by interaction at the edges vide equation 5. Hence if chemical bonds were

involved in the interactions, as visualized above, nicotine would be lost on heating in steps, that being bound in the interlayer being the last to undergo decomposition. With this end in view it was considered worthwhile to investigate the interaction of nicotine with montmorillonite by thermal analysis.

A reference to Figure 14 showed an enhanced endothermic effect at about 275°C followed by two exothermic peaks in the DTA curve of nicotine treated montmorillonite. The deeper endothermic effect at about 275°C appeared to be due to removal of physically adsorbed nicotine formed vide equation 6, the exothermic peak at 450°C due to decomposition of the interlayer nicotinium ions. An interesting observation was provided by a comparative study of the sodium and nicotine saturated DTA curves. The appearance of an exothermic peak in the region devoid of it in Na-saturated montmorillonites was indicative of a chemical reaction that had occurred between sodium clay and nicotine to give a complex ion vide equation 4. The weight loss curves lent further support to the above conclusions. The total weight loss was completed at about 650°C.

In all the systems considered above, it was noticed that as concentration of nicotine increased, the sin curve heights of figures 8 and 9 and dd molecular, which gave an indication of the extent of adsorption of nicotine in clay

as compared to its molecular form in suspension, decreased (Table LXII). These results were indicative of the fact that adsorption was negatively correlated to pH. An examination of the correlation coefficients between adsorption of nicotine and pH of the equilibrium suspensions indicated that at 5% level of significance and 15 degrees of freedom, a good correlation was obtained between pH and percentage of nicotine adsorbed in the case of acid clays as well as the sodium and calcium systems. No such correlation was, however, observed in the case of ammonium and barium montmorillonites.

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CHAPTER IV

A PHYSICO-CHEMICAL STUDY OF THE INTERACTION OF NICOTINIC ACID ESTERS

A PHYSICO-CHEMICAL STUDY OF THE INTERACTION OF MICROLLITE WITH HUMIC ACID

The interaction of organic matter with clays and soils has been extensively studied.[1,2] It has been reported that this interaction with siliceous and aluminous surfaces in dilute suspensions is affected by several factors such as the nature of the organic substance, its solubility and concentration in the solvent, the solvent itself, the lattice configuration of the adsorbent, its saturating cations, CEC, pH, organic matter and orientation of the molecules. Adsorption isotherms have been used to explain some of the interactions.[3,4] Inspite of the study the mechanism of these interactions is doubtful. The confusion, mostly arises as a result of the presence of a large number of chemically active heterogeneous spots in clays in the form of exchangeable cations, sorbed water around cations, hydroxyl groups, lattice surface oxygens and electrical double layer of changing polarity at the edges of the clays. The situation is further complicated by the environmental factors which often simultaneously interact in the reactions. Information on the mechanism of clay-organic interaction is thus very meagre so far as the mineral illite is concerned.

Illite occurs on a large scale in the alluvial soils of India and is an important clay mineral. The fact that this mineral possessed chemically reactive sites at the edges, corners, interlayer and interlattice positions has been visualised by several workers.[5-6] The work of Mitra and Rajagopalan,[7] as well as, Khan and Singhal[8] on the tribasicity of illites is significant in that regard. The use of nicotine and other heterocyclics has been suggested as pesticides. The utility of the investigation on the interactions of nicotine with illite with particular reference to the phenomenon of sorption, therefore, cannot be overemphasised.

The objectives of the present study were, therefore, to investigate the adsorption of nicotine in acid and base saturated illites, study the stoichiometry of the reaction under differing conditions of pH and hence to obtain a more clear understanding of the mechanism of adsorption and the specificity of the different types of sites existing in illitic clays.

EXPERIMENTAL

The clay mineral illite used in the studies was obtained from Wards Natural Science Establishment, Inc. The mineral was from Morris, Illinois and was a sample of the Clay Mineral Standards Project No.49 of the American Petroleum Institute. It was broken up in a mortar using a rubber covered pestle. The

organic matter was oxidised with hydrogen peroxide and the mixture diluted with distilled water. The clay was dispersed by electrical stirring. The suspension obtained was passed through sheets of Whatmann filter paper fitted in the bowl of "International Chemical" Centrifuge at a speed of 9500 rpm to remove any coarse matter. The suspension consisted of $< 2\mu$ clay particles.

Preparation of Na-illite.

The clay suspension was then treated with sodium chloride and dilute hydrochloric acid till the concentration of the supernatent liquid was 2 N with respect to sodium chloride and 0.1 N with respect to hydrochloric acid. The mixture was shaken for half an hour after which the supernatent acid salt solution was removed from the clay suspension by decantation. This treatment was repeated three times and the sodium illite suspension then freed from chloride ions till the clay dispersed and till the conductivity of the suspension was of the same order as that of distilled water (10^{-5}mhos/cm). The suspension was stored in pyrex glassware and used when required.

Preparation of hydrogen saturated illite.

Hydrogen saturated illite with minimal aluminium was freshly prepared vide Aldrich and Buchanan's[9] method from the

suspension by passing it through a column of H-Dowex-50W-X8 cation exchange resin at a speed of 3 cc per minute till the pH and conductance of the suspension became constant. It was then quickly used for potentiometric and conductometric titrations as well as adsorption experiments to avoid any ageing or decomposition of the hydrogen clay. The concentration of the suspension varied from 1.0920 to 1.9530 gm per 100 ml of water.

Preparation of Al^{+3}, Ca^{+2}, Ba^{+2} and NH_4^+ illites.

To obtain the aluminium, calcium, barium and ammonium illites, the sodium clay suspension was treated three times with normal aluminium chloride solution in case of aluminium illite; calcium chloride solution in the case of calcium illite; barium chloride solution in the case of barium illite and ammonium chloride solution in the case of ammonium illite. The suspensions were then washed with distilled water till the resistance in each case was of the same order as that of distilled water (10^{-5}mhos/cm). The suspensions contained approximately 1.2 to 2.5 gm of clay per 100 ml of water in each case.

Determination of concentration of suspensions.

The concentration of each of the suspensions used for potentiometric and conductometric titrations as well as adsorption experiments was determined by evaporating 5 ml of each of

the suspension in the petri dish of known weight and drying the residue at 105° C and finally determining the weight of the residue.

Preparation of nicotine and other solutions.

Nicotine was purified by distilling it at a temperature of 90° C and 4 mm pressure in an inert atmosphere. A standard solution of nicotine was prepared by dissolving 0.20 gm of nicotine and making up the solution 100 ml with double distilled water. Since the solution had a tendency to undergo decomposition, it was freshly prepared every time before use.

A standard solution of hydrochloric acid of the same strength as nicotine was also prepared as per the usual method.

Set 1.

POTENTIOMETRIC AND CONDUCTOMETRIC TITRATIONS

Freshly prepared samples of acid saturated illite and base saturated illites were used for potentiometric and conductometric studies. The time interval between the preparations of hydrogen saturated illite and each titration was kept as minium and uniform as possible to avoid the effects of aluminium movements in hydrogen saturated illite.

Standard solution of sodium hydroxide was used as titrant in case of hydrogen saturated illite. To titrate it 50.00 cc of the suspension was taken in several pyrex glass tubes. To each of these tubes varying amount $\frac{N}{9.68}$ NaOH were added and suspension stirred occasionally for three hours before recording pH and conductance.

To titrate acid and base saturated illite suspensions; standard nicotine was used as titrant. To 10.0 cc of each of the suspensions taken in a number of pyrex glass tubes varying amounts of nicotine (0.1 gm nicotine per 100 ml water) solution were added and the suspensions stirred occasionally for three hours before recording pH and conductance. The stirring time and total time for all the titrations was kept as uniform as possible.

The pH readings were recorded with Beckman pH meter

model C, with saturated calomel and glass electrode assembly. Conductivity measurements were carried out with the help of Philip's conductivity meter with dip type cell.

The cation exchange capacity values of the clays and their binary mixtures were evaluated from the inflection points in their titration curves.

The results obtained for pH and conductivity measurement with sodium hydroxide are given in table LXIV and represented vide figures 15 and 16 by dotted curves. Similarly the results obtained for pH and conductivity measurements of acid and base saturated illites with nicotine are given in tables LXV to LXX and represented vide figures 15 and 16, curves 1 to 3.

Set 1.

Table LXIV

Potentiometric and conductometric titrations of hydrogen saturated illite with sodium hydroxide.

Concentration of clay in potentiometry = 0.5035 gm/50 ml

Concentration of clay in conductometry = 0.5450 gm/50 ml

Volume of suspension used = 50.0 ml

Strength of NaOH = $\frac{N}{9.65}$

Meq.of alkali per 100 gm	pH of the mixture	Meq.of alkali per 100 gm	Conductance x 10^5 mho
0.00	3.00	0.00	12.66
3.54	3.00	7.56	10.99
7.08	3.20	9.45	9.09
10.62	3.50	11.34	7.69
12.39	3.75	13.23	6.25
14.16	4.00	15.12	5.55
15.93	4.60	17.01	5.55
17.70	5.40	18.90	5.88
19.47	5.92	22.68	6.90
21.24	6.50	26.46	10.50
23.01	7.70	30.24	17.24
24.78	8.75	34.02	25.64
26.55	9.30	37.80	35.71
28.32	9.75	47.24	64.58
31.86	10.10	56.70	90.91
35.40	10.30	66.25	122.00

Table LXV

Potentiometric and conductometric titrations of hydrogen saturated illite with nicotine.

Concentration of clay = 0.1564 gm/10 ml

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 1.5072 gm/250 ml

Volume of nicotine in ml	Volume of water added in ml	Meq. of nicotine per 100 gm clay	pH of the mixture	Conductance x 10^5 mhos.
0.0	4.0	0.00	3.00	10.53
0.1	3.9	2.33	3.00	8.71
0.2	3.8	4.66	3.20	0.19
0.3	3.7	6.99	3.35	7.14
0.4	3.6	9.32	3.62	4.76
0.5	3.5	11.65	4.60	3.07
0.6	3.4	13.98	4.75	2.77
0.7	3.3	16.31	5.60	2.70
0.8	3.2	18.64	6.30	2.94
0.9	3.1	20.97	6.68	3.22
1.0	3.0	23.30	7.00	3.70
1.1	2.9	25.63	7.40	3.77
1.2	2.8	27.96	7.55	4.08
1.3	2.7	30.29	8.05	4.16
1.4	2.6	32.62	8.32	4.54
1.6	2.4	37.28	8.32	5.00
1.8	2.2	41.94	8.45	5.26
2.0	2.0	46.60	8.42	5.13
2.5	1.5	58.25	8.45	5.55
3.0	1.0	69.90	8.70	5.88
4.0	0.0	93.20	8.90	6.66

Table LXVI

Potentiometric and conductometric titrations of aluminium saturated illite with nicotine

Concentration of clay = 0.0720 gm/10 ml

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 0.10 gm/100 ml

Volume of nicotine in cc	Volume of water added in cc	Meq. of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.000	5.70	3.66
0.4	19.6	3.424	6.15	4.11
0.8	19.2	6.848	6.90	4.20
1.2	18.8	10.272	6.95	4.20
1.6	18.4	13.696	7.35	4.20
2.0	18.0	17.100	7.75	4.20
2.4	17.6	20.524	8.00	4.11
2.8	17.2	23. 948	8.20	4.11
3.2	16.8	27.372	8.30	4.20
3.6	16.4	30.796	8.50	4.20
4.0	16.0	34.220	8.60	4.38
5.0	15.0	42.800	8.60	4.38
6.0	14.0	51.360	8.65	4.38
7.0	13.0	59.920	8.70	4.53
8.0	12.0	68.440	8.75	4.53
9.0	11.0	77.040	8.75	4.53
10.0	10.0	85.600	8.80	4.53
12.0	8.0	102.720	8.85	4.53
14.0	6.0	119.840	8.90	4.53
15.0	5.0	128.400	8.95	4.53

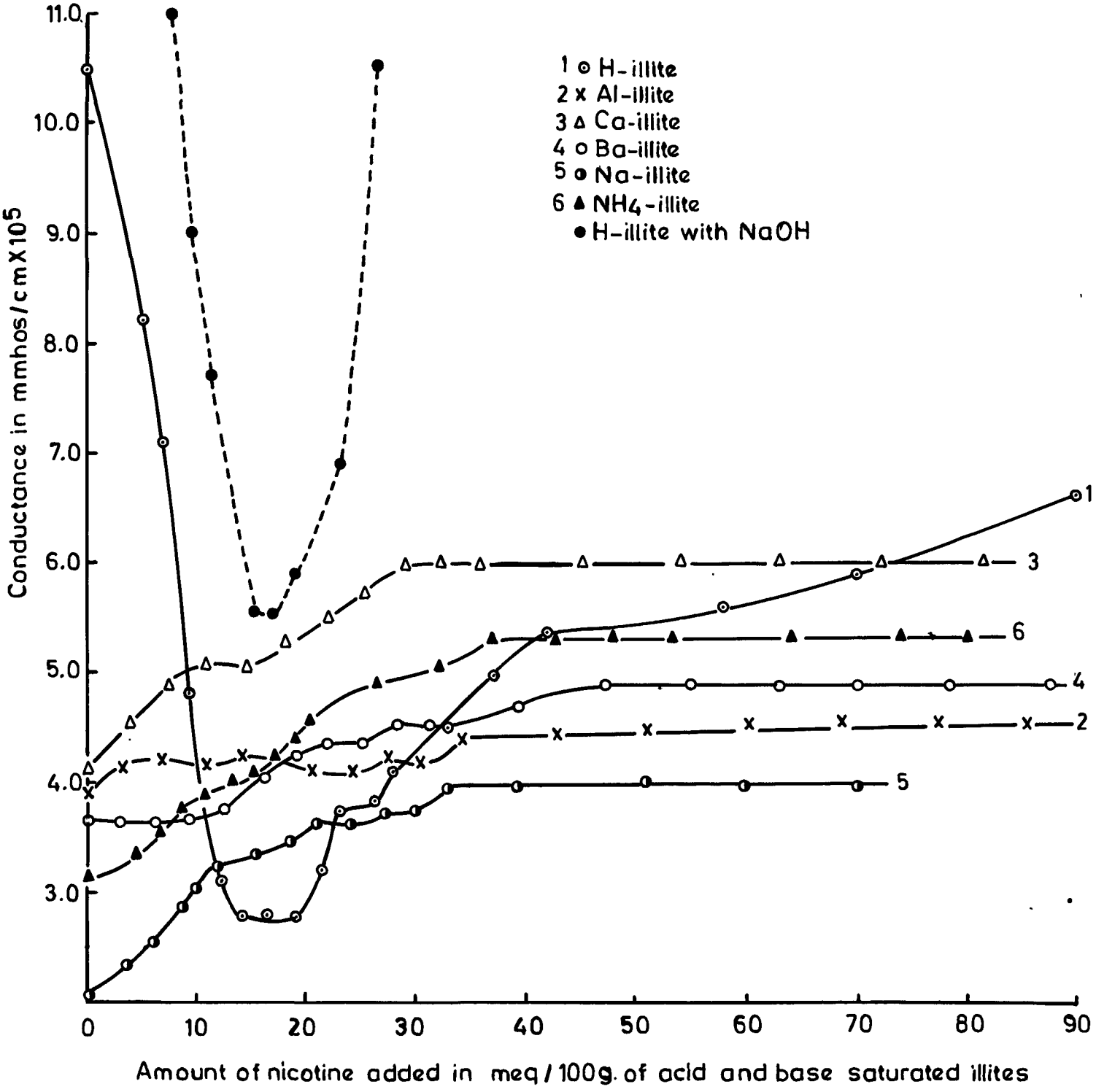


Fig. 15 Conductometric titrations of acid and base saturated illites with nicotine

Table LXVII

Potentiometric and conductometric titrations of sodium illite with nicotine

Concentration of clay = 0.2068 gm/10 ml suspension

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 0.10 gm/100 ml

Volume of nicotine in cc	Volume of water added in cc	Meq. of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.000	5.20	2.06
0.4	19.6	1.192	5.55	2.14
0.8	19.2	2.384	6.00	2.26
1.2	18.8	3.580	6.50	2.38
1.6	18.4	4.790	6.75	2.46
2.0	18.0	5.960	6.90	2.55
2.4	17.6	7.150	7.25	2.69
2.8	17.2	8.340	7.50	2.84
3.2	16.8	9.540	7.75	3.03
3.6	16.4	11.930	7.90	3.24
4.0	16.0	14.900	8.25	3.36
5.0	15.0	17.880	8.40	3.48
6.0	14.0	20.860	8.60	3.53
7.0	13.0	23.840	8.80	3.63
8.0	12.0	26.820	8.90	3.71
9.0	11.0	29.800	9.00	3.75
10.0	10.0	32.780	9.05	3.97
11.0	9.0	35.760	9.10	3.97
12.0	8.0	38.740	9.15	3.97
13.0	7.0	44.700	9.20	3.97
15.0	5.0	50.600	9.20	3.97
17.0	3.0	59.600	9.20	3.97
20.0	0.0	69.800	9.20	3.97

Table XXVIII

Potentiometric and conductometric titrations of calcium illite with nicotine

Concentration of clay = 0.0080 gm/10 ml

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 0.10 gm/100 ml

Volume of nicotine in cc	Volume of water added in cc	m.eq. of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.000	5.25	4.11
0.4	19.6	3.624	6.25	4.59
0.8	19.2	7.248	7.30	4.07
1.2	18.8	10.872	7.80	5.06
1.6	18.4	14.496	8.05	5.26
2.0	18.0	18.120	8.20	5.48
2.4	17.6	21.744	8.30	5.72
2.8	17.2	25.368	8.40	5.98
3.2	16.8	28.992	8.45	5.98
3.6	16.4	32.616	8.45	5.98
4.0	16.0	36.240	8.45	5.98
5.0	15.0	45.300	8.55	5.98
6.0	14.0	54.360	8.65	5.98
7.0	13.0	63.420	8.75	5.98
8.0	12.0	72.480	8.75	5.98
9.0	11.0	81.540	8.80	5.98
10.0	10.0	90.600	8.85	6.22
12.0	8.0	108.720	8.90	6.57
14.0	6.0	126.840	8.95	6.57
15.0	5.0	135.900	8.95	6.57

Table LXIX

Potentiometric and conductometric titrations of barium illite with nicotine

Concentration of clay = 0.0780 gme/10 ml

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 0.10 gm/100 ml

Volume of nicotine in cc	Volume of water added in cc	Meq. of nicotine per 100 gm of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.000	5.05	3.65
0.4	19.6	3.124	5.95	3.65
0.8	19.2	6.248	6.55	3.65
1.2	18.8	9.392	7.35	3.75
1.6	18.4	12.496	7.75	3.98
2.0	18.0	15.620	8.15	4.11
2.4	17.6	18.744	8.35	4.20
2.8	17.2	21.868	8.45	4.38
3.2	16.8	24.992	8.55	4.38
3.6	16.4	28.116	8.55	4.53
4.0	16.0	31.240	8.60	4.53
5.0	15.0	39.050	8.70	4.69
6.0	14.0	46.860	8.80	4.87
7.0	13.0	54.670	8.85	4.87
8.0	12.0	62.480	8.90	4.87
9.0	11.0	70.290	8.95	4.87
10.0	10.0	78.100	9.00	4.87
12.0	8.0	93.720	9.05	4.87
14.0	6.0	109.340	9.10	4.87
15.0	5.0	117.340	9.10	4.87

Table LXX

Potentiometric and conductometric titrations of zirconium illite with nicotine

Concentration of clay = 0.1160 gm/10 ml

Volume of clay suspension taken in different tubes = 10.0 ml

Strength of nicotine = 0.10 gm/100 ml

Volume of nicotine in cc	Volume of water added in cc	Meq. of nicotine per 100 gm. of clay	pH of the mixture	Conductance x 10^5 mhos
0.0	20.0	0.000	5.00	3.13
0.4	19.6	2.124	5.75	3.13
0.8	19.2	4.240	6.20	3.57
1.2	18.8	6.372	7.30	3.55
1.6	18.4	8.496	7.75	3.75
2.0	18.0	10.620	8.00	3.86
2.4	17.6	12.744	8.50	3.98
2.8	17.2	14.868	8.55	4.11
3.2	16.8	16.992	8.55	4.20
3.6	16.4	19.116	8.55	4.30
4.0	16.0	21.240	8.55	4.35
5.0	15.0	26.550	8.60	4.67
6.0	14.0	31.860	8.65	5.06
7.0	13.0	37.170	8.75	5.26
8.0	12.0	42.480	8.85	5.26
9.0	11.0	47.790	8.85	5.26
10.0	10.0	53.100	8.90	5.26
12.0	8.0	63.720	8.95	5.26
14.0	6.0	74.340	9.00	5.26
15.0	5.0	79.650	9.00	5.26

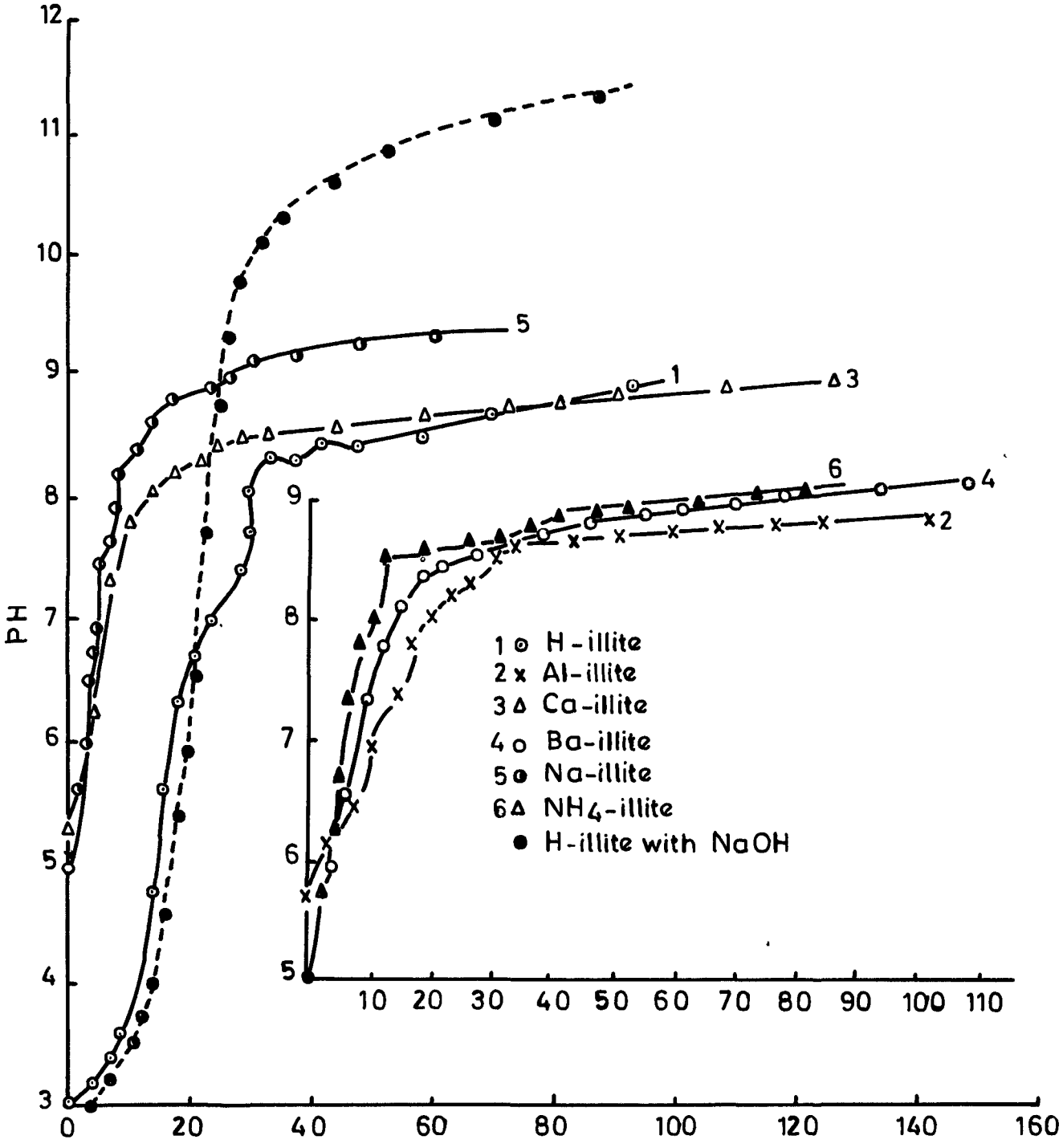


Fig. 16 PH titrations of acid and base saturated illites with nicotine

Set 2.

DETERMINATION OF pK VALUES

The pK values of the acid and base saturated illites were obtained from the titrations curves using the relation:

$$pH = pK + \log \frac{Salt}{Acid},$$

so that at half neutralisation of the first acidity pH was equal to pK_1. Similarly at half neutralisation of the second, and third acidities pH's' at these points were taken as equivalent to pK_2 and pK_3 respectively and were equivalent to the dissociation constants. The results are given in table LXXI.

Table LXXI

Base exchange capacities of the acid and base saturated illites as obtained with potentiometric and conductometric titrations with nicotine in me/100g.clay.

Nature of clay	Potentiometry		
	1st inflection	2nd inflection	3rd inflection
H - illite	15.0 pK_1 3.35	30.0 pK_2 24.65	40.0 pK_3 6.50
Al - illite	10.0	18.0	30.0
Ca - illite	11.5	23.0	-
Ba - illite	11.5	-	-
Na - illite	15.0	24.0	30.0
NH_4 - illite	11.5	-	30.0

(Continuation of Table LXXI)

Base exchange capacities of the acid and base saturated illites as obtained with potentiometric and conductometric titrations with nicotine in me/100g.clay.

Nature of clay	Conductometry			NaOH titration of H-illite only	
	1st inflection	2nd inflection	3rd inflection	Potentiometry	Conductometry
H - illite	15.0	27.0	42.0	pK_1 9.30 21.5	16.0
Al - illite	10.5	22.0	31.0	Only one inflection	
Ca - illite	12.5	-	29.5	is obtained in these	
Ba - illite	11.5	24.0	33.0	cases.	
Na - illite	9.0	15.0	30.0		
NH_4 - illite	16.0	-	32.0		

Set 3.

ADSORPTION OF NICOTINE BY ILLITE

The adsorption experiments were carried out by taking 5.0 ml of the acid and base saturated illite suspensions in a number of pyrex glass stoppered centrifuge tubes and adding varying concentrations of the standard nicotine (0.2 gm per 100 ml water) solution and adjusting the mixture to a constant volume with distilled water. The tubes were fitted on a shaker and shaken for three hours each day for three days at a constant temperature to attain equilibrium. The mixtures were then allowed to sediment overnight, the supernatant liquids taken out, centrifuged and titrated with standard hydrochloric acid using methyl red as indicator to estimate the residual nicotine. The adsorption of nicotine was obtained from the change in concentration of the solution before and after contact with the clay. Curves were plotted between equilibrium concentration of nicotine and moles of nicotine adsorbed per 100 gm of clay. The results are given in tables LXXII (a) to LXXVII (a) and represented vide figure 17 curves 1 to 6.

DETERMINATION OF Kd (Molecular)

The Kd (Molecular)[10] of nicotine in illite suspensions

was calculated from the relation:

$$Kd = \frac{\text{Amount of nicotine per dry gram of illite after equilibrium}}{\text{Amount of nicotine per ml of liquid after equilibrium}}$$

$$Kd = \frac{F-I}{I} \times \frac{\text{Total volume of the suspension}}{\text{Weight of the clay in the suspension}}$$

where F was the volume of nicotine added in ml and I was the volume of nicotine in equilibrium suspension. The results are given in tables LXXII (b) to LXXVII (b) and represented vide figures 18 and 19.

CALCULATION OF CORRELATION COEFFICIENTS

Correlation coefficients between amount of nicotine adsorbed and pH were calculated as per statistical methods of analysis, as more specifically explained under the Chapter of Introduction and given in tables LXXII (b) to LXXVII (b).

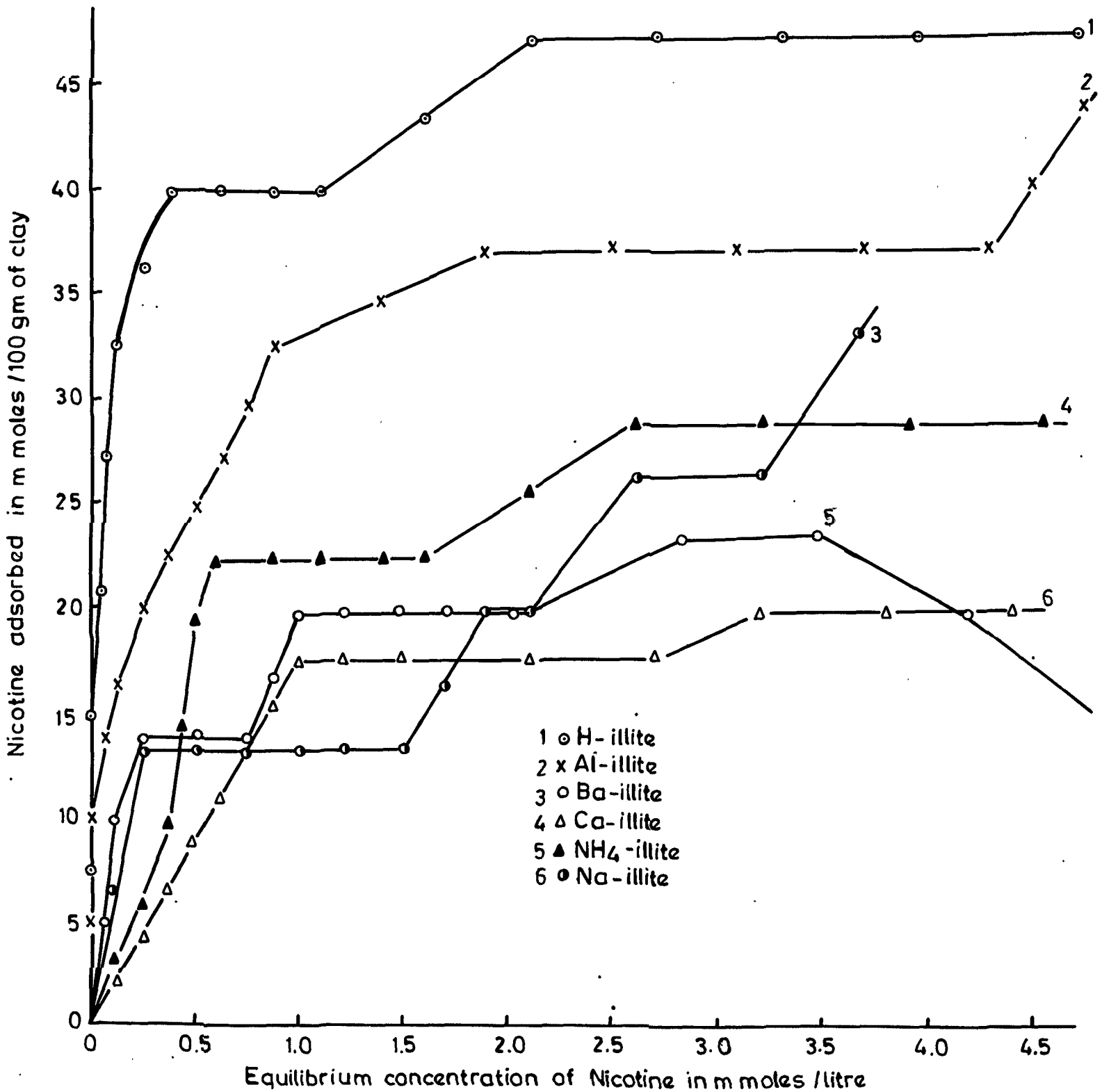


Fig. 17 Adsorption isotherms for the adsorption of Nicotine by acid and base saturated illites

Set 3.

Table LXXII (a)

Adsorption of nicotine by hydrogen saturated illite

(i) Concentration of hydrogen saturated clay suspension = 0.0678 gms/5 ml
(ii) Weight of nicotine = 0.20 gms/100 ml
(iii) Strength of nicotine = Strength of HCl
(iv) Indicator used = Methyl red
(v) Volume of the suspension taken = 5.0 ml
(vi) Total volume of the mixture made upto = 20.0 ml

Volume of nicotine soln added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in n moles/gm clay
0.00	0.00	0.0000	0.00	0.0000
0.40	0.00	0.0000	0.40	0.0724
0.80	0.00	0.0000	0.80	0.1448
1.20	0.05	0.0308	1.15	0.2081
1.60	0.10	0.0616	1.50	0.2715
2.00	0.20	0.1232	1.80	0.3258
2.40	0.40	0.2464	2.00	0.3620
2.80	0.60	0.3696	2.20	0.3984
3.20	1.00	0.6160	2.20	0.3984
3.60	1.40	0.8624	2.20	0.3984
4.00	1.80	1.1088	2.20	0.3984
5.00	2.80	1.8016	2.40	0.4344
6.00	3.40	2.0944	2.60	0.4706
7.00	4.40	2.7104	2.60	0.4706
8.00	5.40	3.3264	2.60	0.4706
9.00	6.40	3.9424	2.60	0.4706
10.00	7.40	4.5816	2.60	0.4706

Table LXXII (b)

(Continuation of table LXXII (a))

Percentage of nicotine adsorbed	Ka (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		3.40
100.00	∞		4.05
100.00	∞		4.75
95.00	6734.50		5.75
93.00	4425.50		6.00
90.00	2647.50		7.05
83.50	1472.50		8.00
70.50	1031.80		8.40
67.30	648.90		8.40
61.90	463.60	r = - 0.228	8.60
55.00	300.20		8.75
48.00	271.70		8.90
43.30	225.50		9.00
37.10	174.20		9.05
32.40	142.00		9.10
28.80	119.80		9.15
26.00	103.60		9.20

Table XXXII (a)

Adsorption of nicotine by aluminium saturated illite

(i) Concentration aluminium clay suspension = 0.0932 gms/5 ml
(ii) Weight of nicotine = 0.20 gms/100 ml
(iii) Strength of nicotine = Strength of HCl
(iv) Indicator used = Methyl red
(v) Volume of the suspension taken = 5.0 ml
(vi) Total volume of the mixture = 20.0 ml

Volume of nicotine soln.added in ml	Volume of HCl required to titrate vacuum dual nicotine in ml	Equilibrium concentration of nicotine in moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in mmoles/gm clay
0.00	0.00	0.0000	0.00	0.0000
0.40	0.00	0.0000	0.40	0.0496
0.80	0.00	0.0000	0.80	0.0992
1.20	0.10	0.0016	1.10	0.1364
1.60	0.20	0.1232	1.40	0.1736
2.00	0.40	0.2464	1.60	0.1984
2.40	0.60	0.3696	1.80	0.2232
2.80	0.80	0.4928	2.00	0.2480
3.20	1.00	0.6160	2.20	0.2728
3.60	1.20	0.7392	2.40	0.2976
4.00	1.40	0.8624	2.60	0.3224
5.00	2.20	1.3552	2.80	0.3472
6.00	3.00	1.8480	3.00	0.3720
7.00	4.00	2.4640	3.00	0.3720
8.00	5.00	3.0800	3.00	0.3720
9.00	6.00	3.6960	3.00	0.3720
10.00	7.00	4.3120	3.00	0.3720

Table LXXXIII (b)

(Continuation of table LXXXIII (a))

Percentage of nicotine ester	Ed (molecular)	Correlation coefficient	pH of the solution
0.00	0.00		5.35
100.00	∞		5.45
100.00	∞		5.55
91.60	2308.40		6.00
87.50	1411.70		6.70
80.00	806.40		7.45
75.00	604.70		7.90
71.40	506.30		8.10
60.10	444.00		8.20
66.60	405.30	r = - 0.571	8.25
65.00	374.10		8.30
56.00	254.50		8.40
50.00	232.00		8.70
42.60	150.00		8.70
37.50	141.10		8.75
33.33	91.70		8.80
30.00	86.90		9.00

Table LXXIV (a)

Absorption of nicotine by sodium illite

(i) Concentration of sodium clay suspension = 0.0370 gm/5 ml
(ii) Weight of nicotine = 0.20 gm/100 ml
(iii) Strength of nicotine solution = Strength of HCl soln
(iv) Indicator used = Methyl red
(v) Volume of suspension taken = 5.0 ml
(vi) Total volume of the mixture = 20.0 ml

Volume of nicotine soln.added	Volume of HCl required to titrate acid nicotine in ml	Equilibrium concentration of nicotine in moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in moles/gm clay
0.00	0.00	0.0000	0.00	0.000
0.40	0.20	0.1232	0.20	0.066
0.80	0.40	0.2464	0.40	0.132
1.20	0.80	0.4928	0.40	0.132
1.60	1.20	0.7392	0.40	0.132
2.00	1.60	0.9856	0.40	0.132
2.40	2.00	1.2320	0.40	0.132
2.80	2.40	1.4784	0.40	0.132
3.20	2.70	1.6632	0.50	0.165
3.60	3.00	1.8480	0.60	0.198
4.00	3.40	2.0944	0.60	0.198
5.00	4.20	2.5872	0.80	0.264
6.00	5.20	3.2032	0.80	0.264
7.00	6.00	3.6960	1.00	0.333
8.00	6.80	4.1888	1.20	0.396
9.00	7.60	4.6816	1.40	0.462
10.00	8.40	5.1744	1.60	0.528

Table LXXIV (b)

(Continuation of table LXXIV (a)).

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		5.10
50.00	195.10		6.10
50.00	195.10		7.50
33.33	96.30		8.10
25.00	64.50		8.20
20.00	48.40		8.35
16.60	39.40		8.45
14.20	32.20		8.50
14.00	34.90		8.50
16.60	36.70	r = - 0.241	8.60
15.00	34.20		8.65
15.00	37.20		8.70
13.20	25.00		8.80
14.00	32.20		8.85
15.00	34.10		9.00
15.50	36.00		9.00
16.00	36.70		9.00

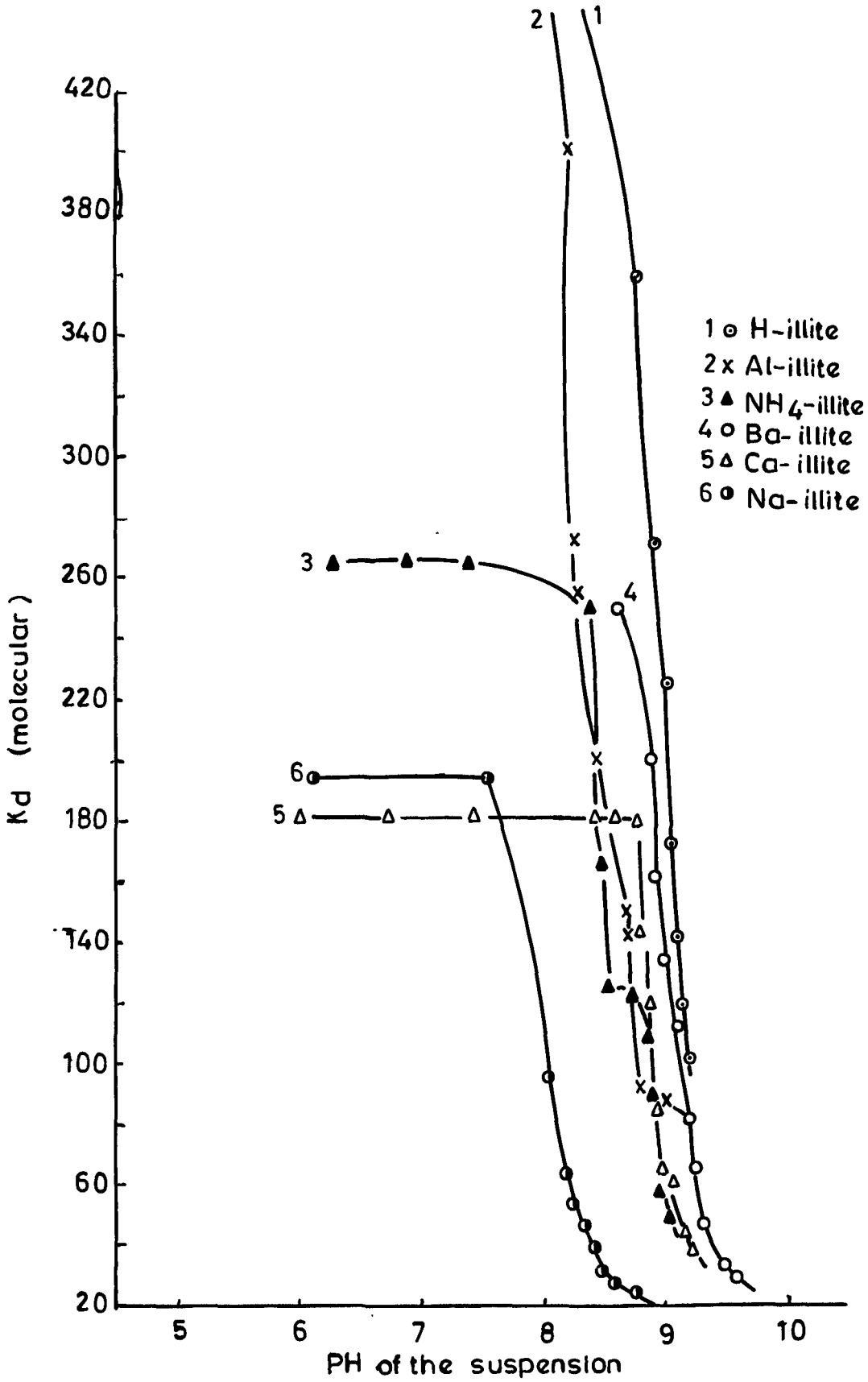


Fig. 18 Variation in distribution coefficient (molecular) with PH of the illite suspension

Table XXXV (a)

Adsorption of nicotine by calcium illite

(i) Concentration of calcium clay suspension = 0.1109 gms/5 ml

(ii) Weight of nicotine = 0.20 gms/100 ml

(iii) Strength of nicotine solution = Strength of .01

(iv) Indicator used = Methyl red

(v) Volume of the suspension taken = 5.0 ml

(vi) Total volume of the mixture = 20.0 ml

Volume of nicotine soln. added in ml	Volume of .01 N HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in moles/gm clay
0.00	0.00	0.0000	0.00	0.000
0.40	0.20	0.1232	0.20	0.022
0.80	0.40	0.2464	0.40	0.044
1.20	0.60	0.3696	0.60	0.066
1.60	0.80	0.4928	0.80	0.088
2.00	1.00	0.6160	1.00	0.110
2.40	1.20	0.7392	1.20	0.132
2.80	1.40	0.8624	1.40	0.154
3.20	1.60	0.9856	1.60	0.176
3.60	2.00	1.2320	1.60	0.176
4.00	2.40	1.4784	1.60	0.176
5.00	3.40	2.0944	1.60	0.176
6.00	4.40	2.7104	1.60	0.176
7.00	5.20	3.2032	1.80	0.198
8.00	6.20	3.8192	1.80	0.198
9.00	7.20	4.4352	1.80	0.198
10.00	8.20	5.0512	1.80	0.198

Table LXXV (b)

(Continuation of table LXXV (a)).

Percentage of nicotine adsorbed	Md (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		5.20
50.00	181.80		6.00
50.00	181.00		6.70
50.00	181.80		7.40
50.00	181.00		8.40
50.00	180.50		8.40
50.00	180.40		8.45
50.00	180.60		8.60
50.00	180.70	r = -0.019	8.75
44.40	145.40		8.80
39.90	120.30		8.90
33.70	84.80		8.95
26.60	65.70		9.00
26.70	62.50		9.10
22.50	53.70		9.20
20.00	45.00		9.20
18.00	39.50		9.25

Table LXXVI (a)

Adsorption of nicotine by barium illite

(i) Concentration of the barium clay suspension = 0.0742 gms/5 ml
(ii) Weight of nicotine = 0.20 gms/100 ml
(iii) Strength of nicotine solution = Strength of HCl
(iv) Indicator used = Methyl red
(v) Volume of the suspension taken = 5.0 ml
(vi) Total volume of the mixture = 20.0 ml

Volume of nicotine soln. added in ml	Volume of HCl required to titrate residual nicotine in ml	Equilibrium concentration of nicotine in moles per litre	Nicotine adsorbed in ml	Nicotine adsorbed in moles/gm clay
0.00	0.00	0.0000	0.00	0.0000
0.40	0.10	0.0616	0.30	0.0498
0.80	0.20	0.1232	0.60	0.0996
1.20	0.40	0.2464	0.80	0.1328
1.60	0.80	0.4928	0.80	0.1328
2.00	1.20	0.7392	0.80	0.1328
2.40	1.40	0.8624	1.00	0.1660
2.80	1.60	0.9856	1.20	0.1992
3.20	2.00	1.2320	1.20	0.1992
3.60	2.40	1.4784	1.20	0.1992
4.00	2.80	1.7248	1.20	0.1992
5.00	3.80	2.3408	1.20	0.1992
6.00	4.60	2.8336	1.40	0.2324
7.00	5.60	3.4496	1.40	0.2324
8.00	6.80	4.1888	1.20	0.1992
9.00	8.00	4.9280	1.00	0.1660
10.00	9.00	5.5440	1.00	0.1660

Table LXXVI (b)

(Continuation of Table LXXVI (a)).

Percentage of nicotine adsorbed	Kd (molecules)	Correlation coefficient	pH of the solution
0.00	0.00		6.20
75.00	00.00		7.35
74.00	00.00		8.25
66.00	53.30		8.25
50.00	271.10		8.70
40.00	191.00		8.75
41.30	192.30		8.80
42.90	201.60		8.85
37.90	162.10	r = -0.108	8.90
31.90	134.70		9.00
30.00	114.20		9.10
27.00	85.70		9.15
23.20	62.70		9.20
20.00	67.30		9.25
21.10	48.00		9.30
11.10	33.90		9.50
9.00	29.80		9.60

Table LXXVII (a)

Adsorption of nicotine by ammonium illite

(i) Concentration of ammonium clay suspension = 0.0766 gm/5ml
(ii) Weight of nicotine = 0.20 gm/100 ml
(iii) Strength of nicotine solution = Strength of HCl
(iv) Indicator used = Methyl red
(v) Volume of the suspension taken = 5.0 ml
(vi) Total volume of the mixture = 20.0 ml

Volume of nicotine soln. added in ml	Volume of HCl required to titrate with dual nicotine in ml	Equilibrium concentration of nicotine in m.mole per litre	Nicotine adsorbed in ml	Nicotine adsorbed in m.mole/gm clay
0.00	0.00	0.0000	0.00	0.000
0.40	0.20	0.1232	0.20	0.032
0.80	0.40	0.2464	0.40	0.064
1.20	0.60	0.3696	0.60	0.096
1.60	0.70	0.4312	0.90	0.144
2.00	0.80	0.4928	1.20	0.192
2.40	1.00	0.6160	1.40	0.244
2.80	1.40	0.8624	1.40	0.224
3.20	1.80	1.1088	1.40	0.224
3.60	2.20	1.3552	1.40	0.224
4.00	2.60	1.6016	1.40	0.224
5.00	3.40	2.0944	1.60	0.256
6.00	4.20	2.5872	1.80	0.288
7.00	5.20	3.2032	1.80	0.288
8.00	6.20	3.8192	1.80	0.288
9.00	7.40	4.5584	1.60	0.256
10.00	8.40	5.1744	1.60	0.256

Table LXXVII (b)

(Continuation of table LXXVII (a)).

Percentage of nicotine adsorbed	Kd (molecular)	Correlation coefficient	pH of the suspension
0.00	0.00		5.00
50.00	266.60		6.25
50.00	266.60		6.85
50.00	266.60		7.35
59.40	333.30		7.90
59.90	393.40		8.25
58.50	368.40		8.35
55.00	292.30		8.35
43.70	202.80	r = -0.061	8.40
38.70	166.60		8.50
35.00	127.20		8.55
32.00	123.00		8.75
30.00	110.00		8.85
25.70	90.00		8.90
20.00	65.30		8.95
17.70	61.50		9.00
16.00	50.00		9.05

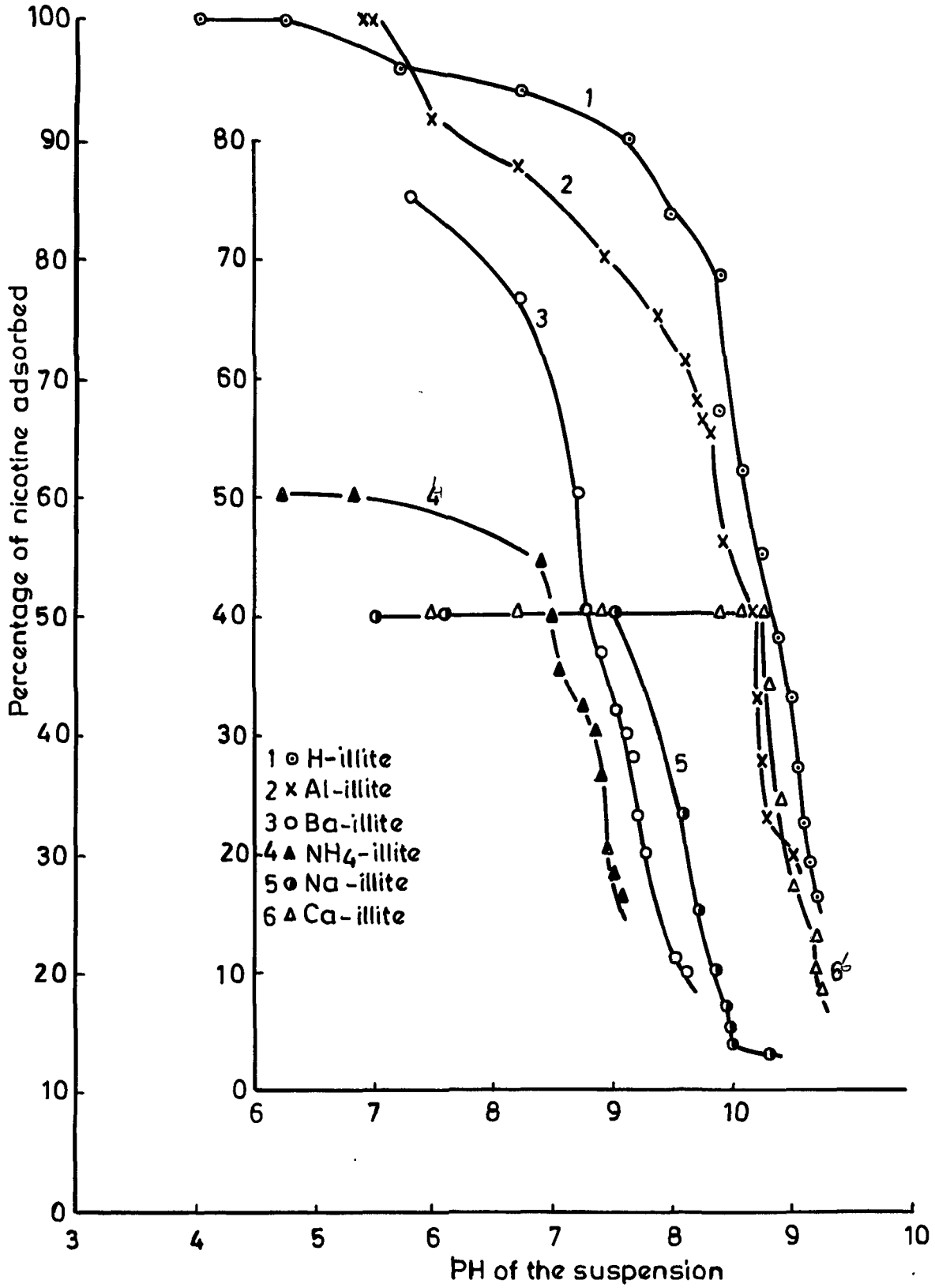


Fig. 19 Effect of PH on the adsorption of nicotine by hydrogen and base saturated illites

Set 4.

X-RAY ANALYSIS

X-ray analysis was carried out on sodium saturated samples of illite, and nicotine treated illites. The nicotine treatment was done upto and three additional concentrations beyond the BEC. For X-ray examination the samples were oriented on glass microslides from a water suspension at room temperature. Patterns were recorded after air drying using filtered Cu K α radiation on a Micrometa goniometer at a speed of 2 degrees per minute. The results are recorded in table LXXVIII, figure 20.

Table LXXVIII

Basal spacings of sodium saturated and nicotine treated illite.

Nature of illite	Nicotine treatment concentration in m.eqlos/100g illite	Basal spacings in A°
Sodium illite		9.4 A°
Nicotine illite	BEC	10.6 A°
Nicotine illite	40	10.6 A°
Nicotine illite	60	10.6 A°
Nicotine illite	80	10.6 A°

Set 5.

DIFFERENTIAL THERMAL ANALYSIS

The apparatus used for the differential thermal analysis of sodium and nicotinium illite sample consisted of a furnace, a specimen block, a specimen holder, a potentiometer, a millivoltmeter, reflecting type galvanometer, resistance, thermocouples and a programme controller. A schematic diagram of the apparatus is presented in figure 21.

The analysis was conducted on the sodium and nicotinium illites. The clays were powdered and then pass through 200 mesh sieve to give a uniform powder and to ensure good packing of the specimen. The samples were dried in vacuum over a saturated solution of $Mg(No_3)_2 \cdot 6\,H_2O$ to ensure the same relative humidity in case of the samples.

Before taking the D.T.A. run, a preliminary study of the effect of heat in the experimental range was made on the clay samples by heating the samples in a silica crucible. The prepared samples were then placed in one of the cavities and the other cavity was filled with α-Al_2O_3. The packing of the materials in the specimen block was made uniform and hard by means of a glass plunger. A differential thermocouple was then connected to the clay specimen and the inert material.

Thermograms were then recorded by carrying out the differential thermal analysis semi-automatically with Leeds

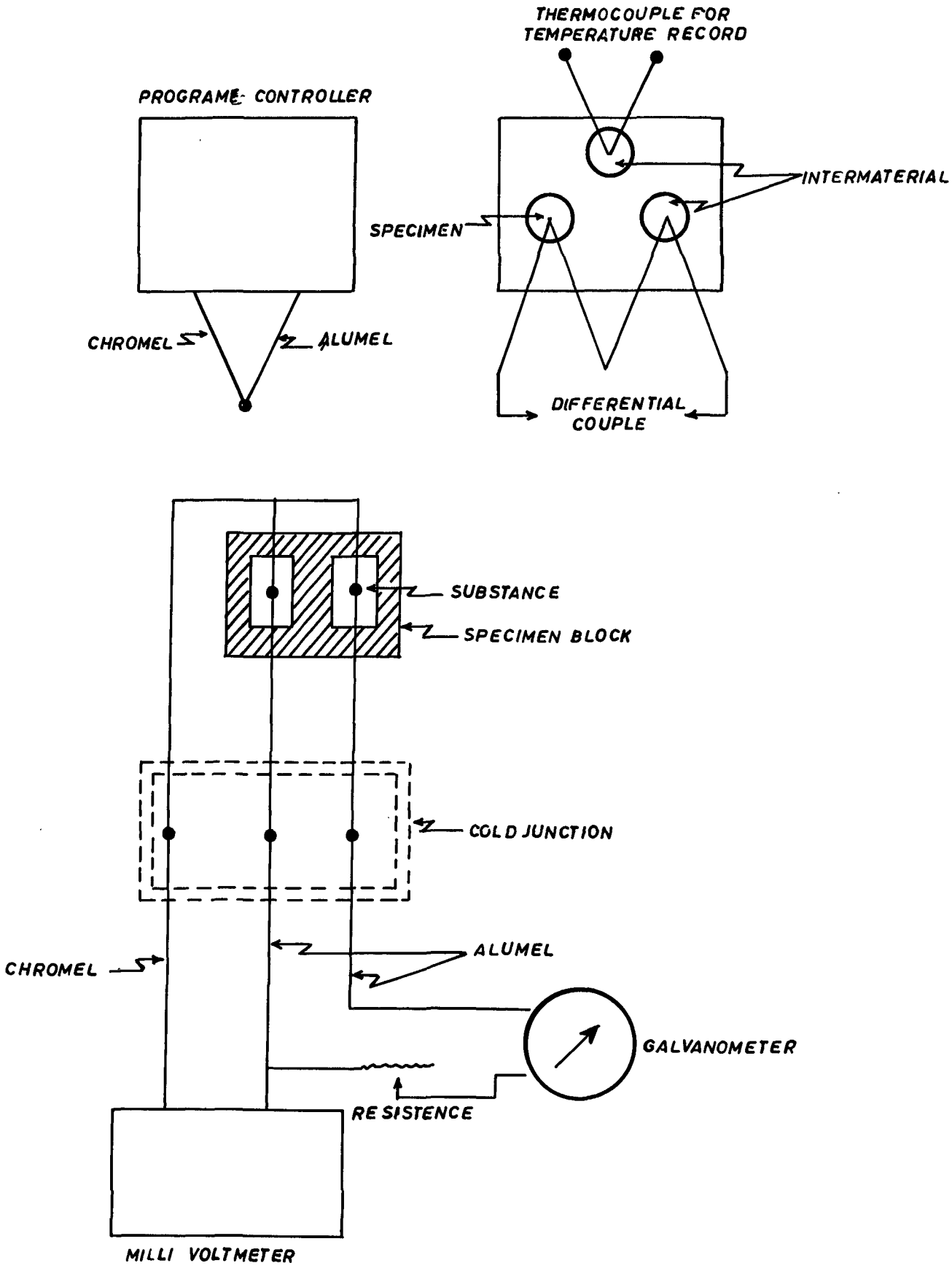


FIG. 21 SCHEMATIC DIAGRAM OF DIFFERENTIAL THERMAL ANALYSIS APPARATUS

and Northrup programme controller which could control the temperature rise at the rate of 10 C per minute. The differential temperature ΔT, was recorded by a sensitive galvanometer using chromel-alumel thermocouple. The temperature, T, of the sample was recorded by a pyrometer. The results obtained were plotted on a graph for various samples and are given in curves 1 and 2 of figure 22. The data is given in tables LXXIX to LXXX.

Table LXXIA

Differential thermal analysis of sodium illite.

Particle size (passed through) = 200 mesh sieve

Inert material = $\alpha - Al_2O_3$

Thermocouple = Chromel-alumel

T	θ	T	θ	T	θ	T	θ
30	0	290	+42	590	+ 69	850	+110
35	- 2	300	+43	600	+ 72	860	+118
50	- 1	310	+45	610	+ 77	870	+120
70	- 3	320	+47	620	+ 80	875	+121
80	- 5	330	+50	630	+ 86	880	+122
90	-10	340	+54	640	+ 90	890	+123
100	-15	350	+61	650	+ 94	900	+124
110	-26	360	+60	660	+ 97		
120	-33	370	+71	670	+100		
130	-26	380	+72	680	+102		
140	- 4	390	+72	690	+104		
145	+ 4	400	+70	700	+105		
150	+10	410	+69	710	+106		
160	+16	430	+70	720	+108		
170	+20	440	+70	730	+109		
180	+25	450	+69	740	+110		
190	+26	460	+69	750	+111		
200	+28	470	+68	760	+111		
210	+32	480	+68	770	+110		
220	+34	490	+67	780	+110		
230	+35	500	+66	790	+108		
240	+37	510	+64	800	+107		
250	+30	520	+62	810	+106		
260	+39	540	+62	820	+105		
270	+39	570	+65	830	+106		
280	+40	580	+68	840	+107		

Table LXXX

Differential thermal analysis of nicotinium illite.

Particle size (pass ed through) = 200 mesh sieve
Inert material = $\alpha - Al_2O_3$
Thermocouple = Chromel-alumel

T	Θ	T	Θ	T	Θ	T	Θ
30	0	310	+ 71	580	+105	850	+110
60	+ 2	320	+ 74	590	+105	860	+120
70	+ 3	330	+ 77	600	+106	870	+122
90	0	340	+ 80	610	+107	880	+125
100	-11	350	+ 83	620	+109	890	+130
110	-46	360	+ 86	630	+108	900	+135
120	-63	370	+ 89	640	+107		
130	-75	380	+ 90	650	+107		
135	-68	390	+ 92	670	+105		
140	-10	400	+ 95	680	+104		
150	+16	410	+ 97	690	+105		
160	+25	420	+ 98	700	+106		
170	+34	430	+100	710	+107		
180	+42	440	+103	720	+108		
190	+46	450	+104	730	+110		
200	+51	460	+107	740	+112		
210	+52	470	+109	750	+114		
220	+50	480	+110	760	+115		
230	+47	490	+109	770	+116		
240	+47	500	+107	780	+116		
250	+50	510	+106	790	+117		
260	+52	520	+105	800	+117		
270	+55	540	+106	810	+118		
280	+57	550	+105	820	+119		
290	+60	560	+106	830	+118		
300	+66	570	+105	840	+118		

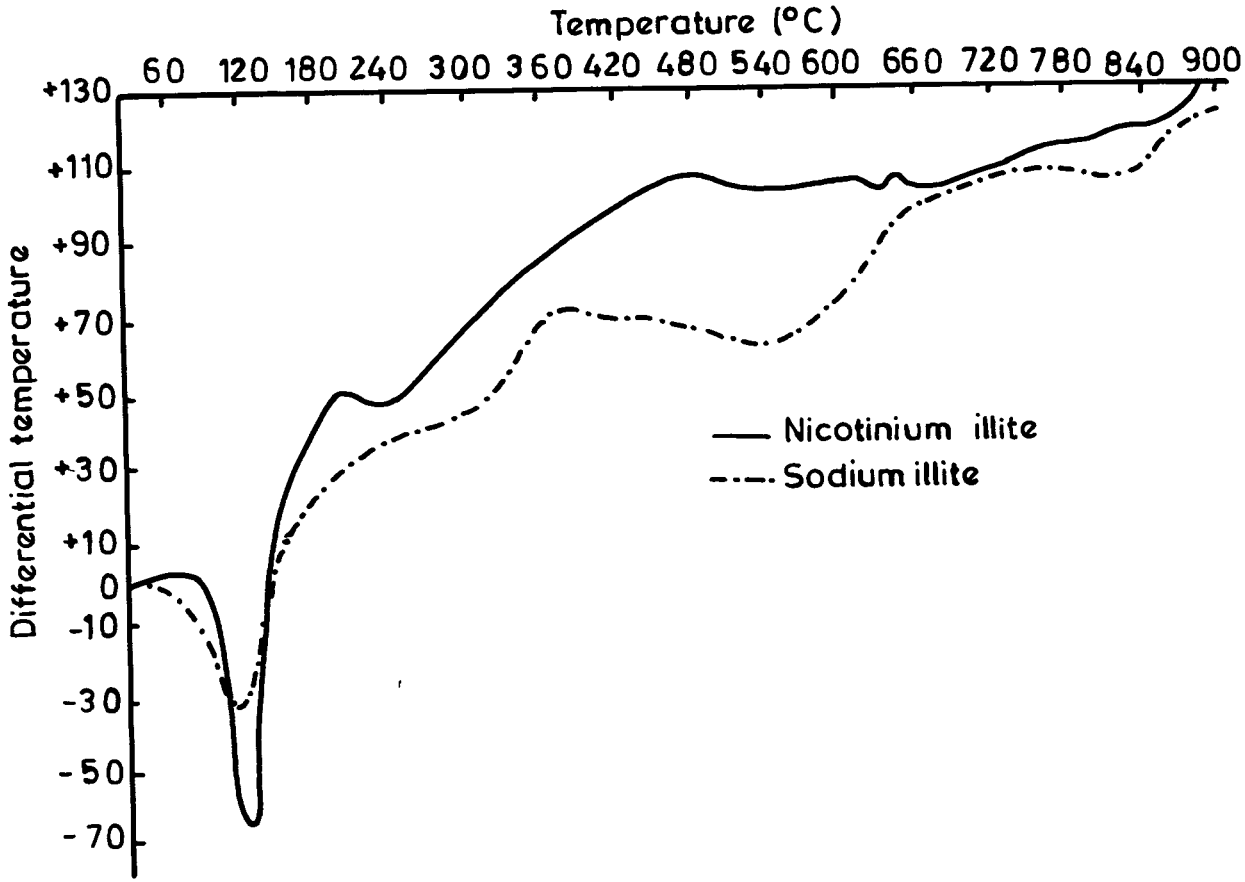


Fig. 22 Differential thermal curves of sodium and nicotinium illites

RESULTS AND DISCUSSION

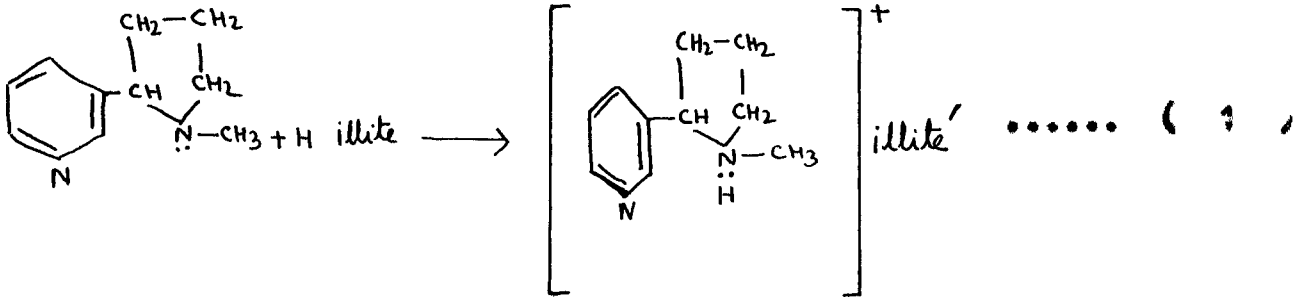
To suitably characterise the illites, the acid and base saturated illites were subjected to conductometric and potentiometric titrations. The results are summarised in table LXXI and represented vide figures 15 and 16 and curves 1 to 6.

An examination of the electrical conductance curves showed a sharp fall in the conductivity of hydrogen illite on addition of nicotine followed by a rapid rise with three inflections. Such inflection points occurred in the conductance studies of some of the base saturated illites also with the difference that the curves exhibited a gradual rise from the very beginning of the titrations. Potentiometric studies also revealed a similar behaviour with the occurrence of three breaks at different pH values, vide figure 16, curves 1-6. The inflection points in the curves were taken as a measure of the base exchange capacity of illites. Generally the ratio of the B.C at three inflection points came out to be nearly 1 : 2 : 3 in both the conductometric as well as the potentiometric studies. The mineral illite thus appeared to behave as a tribasic acid. Evaluation of the dissociation constants at the first, second and third inflection points gave pK_1, pK_2 and pK_3 as 3.35, 4.85 and 6.50 respectively for the hydrogen illite. The above data pointed to the existence of at least three chemically reactive spots on the

illite surfaces, each associated with a different energy level. These reactive sites appeared to be the exchangeable cations including H or K ions as well as the weakly acid octahedral hydroxyls at the interlayer sites, at edges, and at intralattice positions. As the nicotine interacted with these spots, inflections occurred, one after another, the intralattice interaction being the last to occur on account of the time taken by the nicotine molecules to slowly diffuse to the interstitial positions.

The results of adsorption of nicotine by the above suspensions (1.2 to 2.5% V/V) in the concentration range of 0 to 5.0 moles of nicotine per litre are represented by isotherms (Figure 17, Curves 1-6). The curves exhibited three inflections with flat plateaus at 3 and 4 ions. Such complexities in adsorption isotherms with occurrence of inflections and plateaus though not common, have been observed by several workers[11,12] in solute-solute-solvent systems when they underwent complete saturation. An examination of the isotherms given in Figure 17, curves 1-6 showed a well marked difference in the adsorption of nicotine by hydrogen and aluminium saturated illites as compared to that of the base saturated systems. The initial parts of the isotherms of the acid saturated illites exhibited a sharp rise with a vertical curve till ab at the first inflexion was reached (Table LXI). Here the nicotine seemed to possess such a high affinity for the systems that in dilute solutions

it was completely adsorbed. This happened up to a pH value of 5.0 with infinite value of Kd molecular (table XXXXI). This process of chemisorption at low pH appeared to be due to the protonation of the nicotine molecule by hydrogen ions available either in the suspension on the clay surface, followed by adsorption of the nicotine cation either on the lateral surface or the outer surface of illites such as edges and corners. X-ray data showing an increase in basal spacing from 9.4 to 10.6Å°, vide table XXXXII, however, rules out any substantial adsorption at the lateral surface. The reaction with hydrogen illite could be represented as

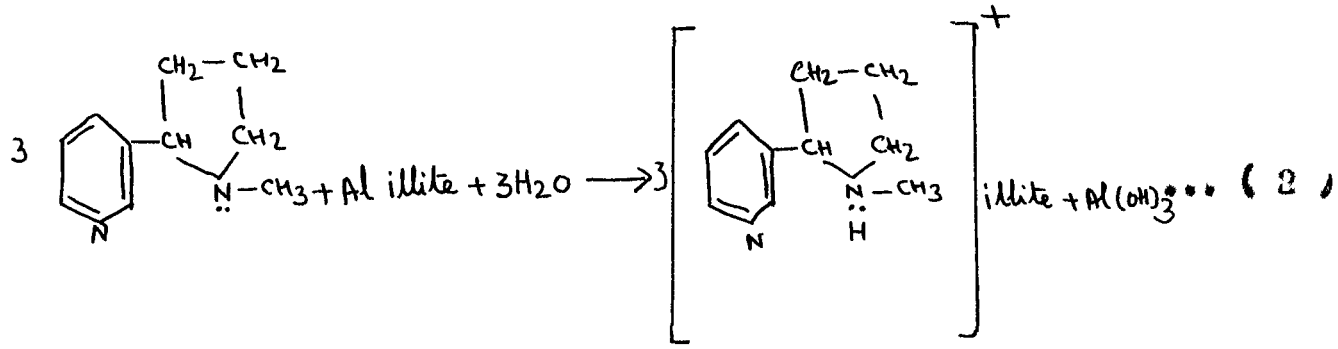


..... (1)

the protonation occurring at the more basic pyrrolidine ring nitrogen of the nicotine molecule.

The aluminium illite, on the other hand, acting more or less as a Bronsted acid[13] in dilute suspensions at a low

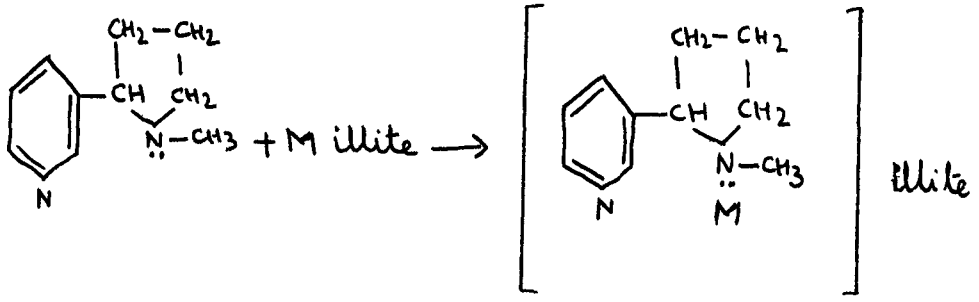
H, adsorbed nicotine according to the following equation:



Those proportions were found to be in accordance with the pH and conductance observations. Thus, the increase in pH was due to elimination of protons from the exchangeons. That there was formation of a nicotinium ion with lower mobility was accounted for by a decrease in conductance on the addition of nicotine to hydrogen illite (Figures 15-16, Curves 1-2). That the above interaction continued, though with reduced intensity was apparent from the rapid rise in the adsorption isotherms (Figure 17, Curves 1-2) beyond the limit mobility. When all the protons had been removed as indicated by the above equation, the conductance and pH both became constant once more but a lower rise in conductance associated with the nicotinium ion.

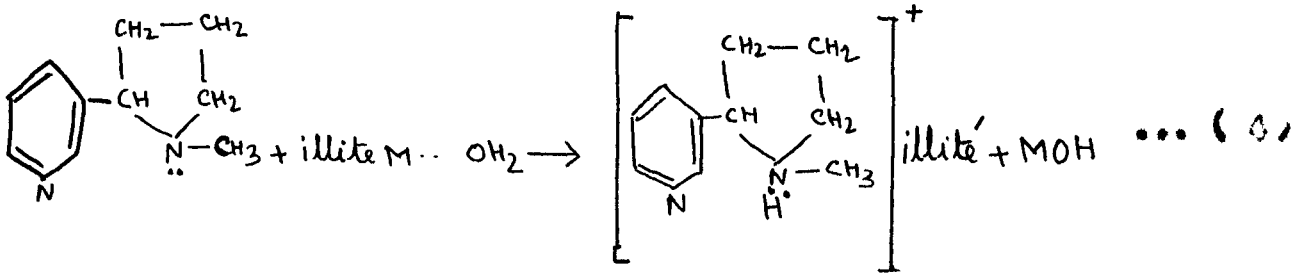
A high initial affinity of nicotine for the base saturated systems viz., ammonium, sodium, calcium and barium illites was also observed but the adsorption forces apparently weaker, so that complete adsorption of nicotine did not occur at any stage. Also the first inflection in the adsorption

isotherms occurred at a much lower value. The adsorption at the first inflection followed the order $K^{+} > Al^{+++} > NH_4^{+} > Ba^{++} > Ca^{++} > Na^{+}$ (Figure 17). Reduced adsorption in base saturated systems appeared to be due to non-availability of protons in base saturated illites at higher pH values (7.5 and higher) and a reduction in molecular surface on base saturation. The results were in agreement with the observations of Mayes, Stacey and Thompson[14] on the adsorption of triazines in humic acids. In analogy with the interactions of some organic bases with the exchangeable cations in bentonites it appeared, that the adsorption in these systems was partly due to formation of coordination bonds, such as,



... (3)

and partly due to the capacity of the nicotine to detach water from around the cations giving rise to proton transfer and formation of nicotinium ions and hydroxide in the interlayer



... (4)

The possibilities of such coordination and proton transfers in

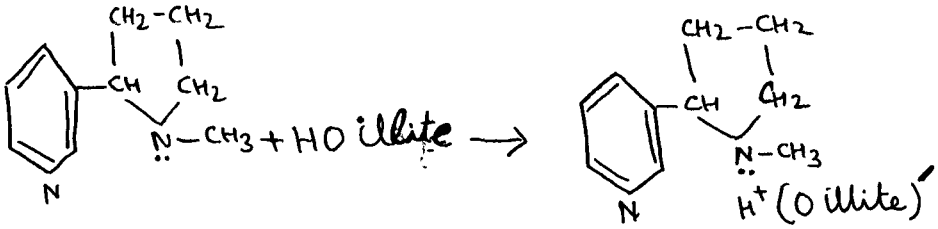
clay systems have also been advocated by several workers.[15,16,17] That such reactions occurred found confirmation in these investigations. Thus, the increase in conductance and pH observed on addition of nicotine to base saturated systems were in accordance with the coordinating power of the exchangeable cations and the formation of basic hydroxides observed vide equation (3) and (4) respectively.

In all the cases considered above, as the initial adsorptive forces were saturated, an inflection occurred and the curves changed their direction. In spite of all efforts to attain equilibrium, the discontinuities in the isotherms persisted. The curves were reproducible except for small deviations of 1 to 2 moles in the amount of nicotine adsorbed by the clay. The inflections followed by plateaus were a pointer that the first stage of saturation was being completed with the formation of a monolayer of nicotine ions on the most active sites of illites, which could or could not be closed packed.

The subsequent rise in adsorption beyond the first plateau, which was quite substantial, was indicative of the formation of a fresh surface or surfaces on the illite layers after the high energy barrier[18] for initial adsorption had been overcome by nicotine molecules.

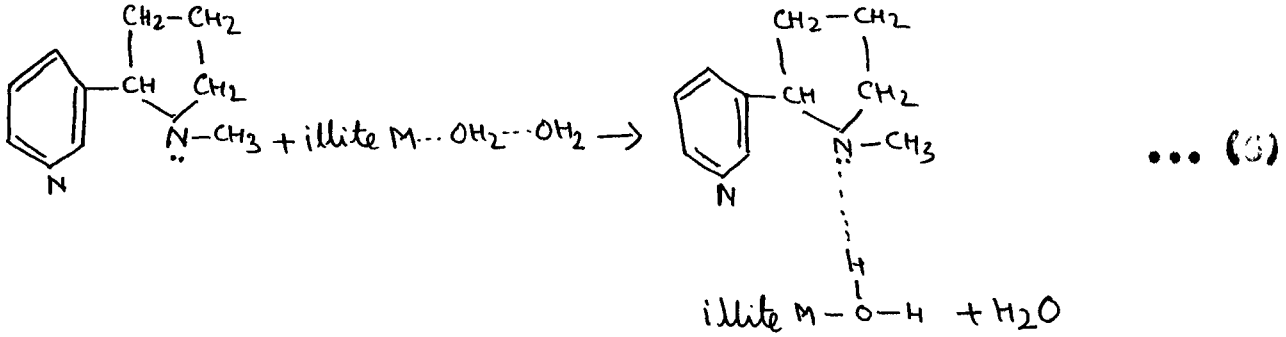
The other effects which also seemed to predominate in this concentration range appeared to be (i) the diffusion of

the nicotine molecules from the lateral surface to interlattice positions and reaction with interlattice hydroxyls as follows:



... (5)

and (ii) dissociation of bonded water from around the mono and divalent cations and formation of hydrogen bonds with the directly coordinated water.



... (6)

Further evidence for some of the above interactions was obtained by differential thermal analysis. It had been suggested that when an organic molecule was strongly attached to a clay surface by chemical bonds, it was retained to a sufficiently high temperature.[19] Due to structural differences the nicotinium ions formed via equations 3 and 5 would not be

so accessible to oxidation as the ions formed vide equations 1, 2, 4 and 6. Hence if chemical bonds were involved in the interactions, as visualised above, nicotine would be lost on heating in stages, that being bound by coordination bonds and that in the interlattices being the last to undergo decomposition. With this end in view it was considered worthwhile to investigate the interaction of nicotine with illite by thermal analysis.

A reference to Figure 22 showed an enhanced endothermic effect at about 130°C followed by two exothermic peaks in the DTA curve of nicotine treated illite. The deeper endothermic effect at 130°C appeared to be due to the removal of physically adsorbed nicotine. The exothermic peak at 210°C due to decomposition of nicotinium illite at the edges and corners while the one at 460°C due to decomposition of interlattice nicotinium ions. The endothermic effect at 620°C was for OH water loss in illite. An interesting observation was provided by a comparative study of the sodium and nicotine saturated DTA curves. The appearance of exothermic peaks in the region devoid of them in sodium saturated illite was indicative of the chemical reactions that had occurred between the sodium clay and nicotine, to give complex ions vide equations given above.

In all the systems considered above it was noticed that as the concentration of nicotine increased, the pH also increased (Figure 16) and Kd molecular which gave an indication

Table LXXXI

Adsorption of nicotine by acid and base saturated illites at different equilibrium concentrations and the correlation coefficients between pH and adsorption.

Sample	pH	Equilibrium concentration in m mol-eq/litre	Amount adsorbed in meq/100 gm clay	% adsorbed	Correlation coefficient	Kd
H-clay	4.20	0.0000	8.50	100.00		
	4.90	0.0000	15.00	100.00		
	5.50	0.0375	19.50	97.00		7300.00
	7.50	0.1000	31.50	91.00	r=-0.228	3010.00
	8.50	0.7500	39.04	64.50		556.25
	9.00	2.0944	47.06	43.30		225.50
Al-clay	4.20	-	-	-		-
	4.90	-	-	-		-
	5.50	0.0000	7.00	100.00	r=-0.571	
	7.50	0.2500	20.00	80.00		406.40
	8.50	1.5000	35.50	55.00		228.50
	9.00	4.3120	57.20	30.00		86.90
Na-clay	4.20	-	-	-		-
	4.90	-	-	-		-
	5.50	0.0050	2.50	50.00	r=-0.241	195.10
	7.50	0.2464	13.20	50.00		195.10
	8.50	1.6600	16.50	14.80		34.90
	9.00	4.1800	39.60	15.00		34.10
NH_4-clay	4.20	-	-	-		-
	4.90	-	-	-		-
	5.50	-	-	-	r=-0.061	-
	7.50	0.2600	10.50	48.50		266.60
	8.50	1.6000	22.50	38.70		166.60
	9.00	4.5500	28.80	17.70		61.50
Ca-clay	4.20	-	-	-		-
	4.90	-	-	-		-
	5.50	0.0750	1.25	50.00		181.80
	7.50	0.3750	6.50	50.00	r=-0.019	181.80
	8.50	0.7500	13.50	50.00		181.80
	9.00	1.0000	17.50	26.60		84.80
Ba-clay	4.20	-	-	-		-
	4.90	-	-	-		-
	5.50	-	-	-		-
	7.50	0.0650	6.00	75.50	r= .108	80.80
	8.50	0.1750	11.50	58.00		62.20
	9.00	1.4784	19.50	31.90		134.70

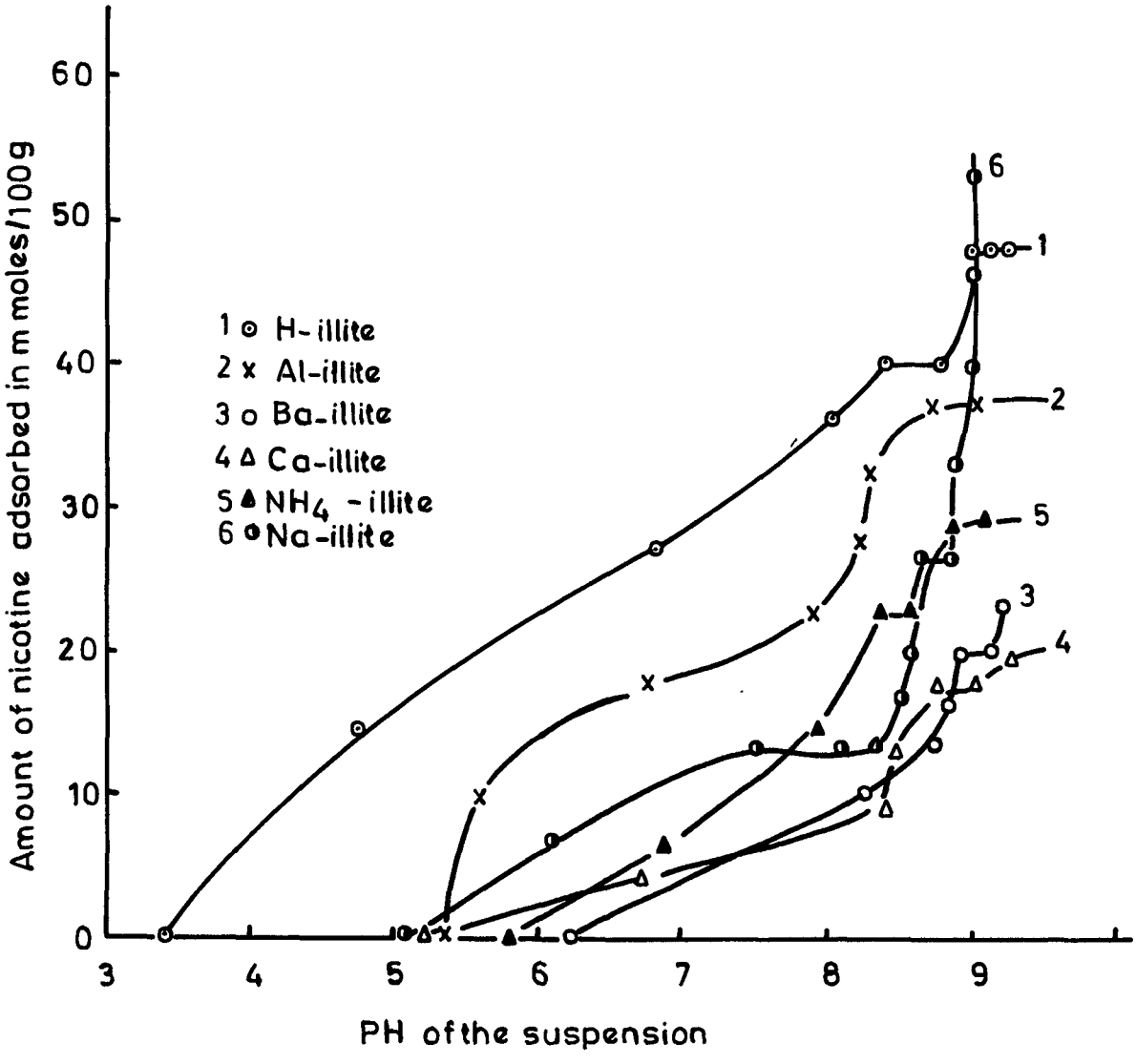


Fig. 23 Effect of PH on the adsorption of nicotine by acid and base saturated illites

of the extent of adsorption of nicotine in illite as compared to its molecular form in suspension decreased (Table LXXXI). The effect of the amount of the nicotine adsorbed on pH of the suspension is given vide Figure 25. An examination of the correlation coefficients between the percentage of nicotine adsorbed and pH of the equilibrium suspension indicated that at 5% level of significance and 15 degrees of freedom a good correlation existed between pH and percentage of nicotine adsorbed in case of acid saturated system as well as sodium illite.

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CHAPTER V

THERMODYNAMICS OF COBALT(II)-HOMOIONIC EXCHANGE ON MONTMORILLONITE CLAY

THERMODYNAMICS OF COBALT(II)-SODIUM EXCHANGE ON MONTMORILLONITE CLAY

The ion exchange mechanism on clays can be made thermodynamically exact if the thermodynamic parameters involved in the system are evaluated with the help of experimental data. El-sayed, Burau and Babcock[1] have obtained the exchange constants for the copper(II)-calcium exchange system on bentonite clay using the thermodynamic formulation of ion exchange equilibria, developed by Argersinger[2] and later on by Gaines and Thomas.[3] They have, however, used the system involving the cations having the same valency and the same ion size parameter (Cu(II)-Ca(II)), so that the correction for solution preference was not considered. We have taken the system cobalt(II)-sodium and, therefore, activity coefficients were obtained to take into account the solution preference.[4,5]

E X P E R I M E N T A L

The clay mineral used in these investigations was montmorillonite, collected by Dr.Ralph J.Holmes and verified under his direction in the mineralogical laboratories of the Columbia University by comparison with the original

samples from Amori, Mississipi. It was a monomineralic sample of the American Petroleum Institute's Project No.49. The sample was obtained from Wards Natural Science Establishment,Inc., Rochester,U.S.A. It was broken up in a mortar using a rubber covered pestle. The organic matter was oxidised with hydrogen peroxide and the mixture diluted with distilled water. The clay was then dispersed by electrical stirring. The suspension obtained was passed through sheets of Whatmann filter paper fitted in the bowl of "International Chemical" centrifuge at a speed of 3500 rpm to remove any coarse matter. The suspension consisted of $< 2\mu$ clay particles.

Preparation of Na-montmorillonite

The clay suspension was then treated with sodium chloride and dilute hydrochloric acid till the concentration of the supernatent liquid was 2N with respect to sodium-chloride and 0.1N with respect to hydrochloric acid. The mixture was shaken for half an hour after which the supernatent acid salt solution was removed from the clay suspension by decantation. This treatment was repeated three times and the sodium clay suspension then freed from chloride ions till the clay dispersed and till the conductivity of the suspension was of the same order as that of distilled water 10^{-5} mhos/cm. The suspension was stored in pyrex glassware and used when required. The pH of the suspension was adjusted by dilute

HNO_3 to a value of 4.0 in each case.

Determination of the concentration of the suspension

The concentration of the suspension used for experiments was determined by evaporating 5 ml of the suspension in a petri dish of known weight and drying the residue at 105°C and finally determining the weight of the residue.

Reagents used in exchange studies

40% Sodium citrate, 2N HCl, 1N HCl, 2N NaOH, 30% H_2O_2, 1-nitroso-2-naphthol, Chloroform, $\frac{N}{250}$ Cobalt nitrate, Sodium and Cobalt standards.

PROCEDURE FOR COBALT(II)-SODIUM EXCHANGE

The cobalt(II)-sodium exchange experiments were carried out by taking 10.0 ml of the sodium montmorillonite clay suspension in stoppered test tubes and adding varying concentrations of $\frac{N}{250}$ cobalt nitrate solution and adjusting the mixture to a constant volume by adding distilled water. The tubes were fitted on a water bath at 40 $\pm$ 1 °C in the first set of experiments and 60 $\pm$ 1 °C in the second set of experiments and shaken for one hour in each case. The mixtures were then centrifuged immediately and the sodium and cobalt in the supernatent liquids were estimated. The sodium was estimated by flame photometer method and cobalt spectrophotometrically by 1-nitroso-2-naphthol[6] as colour reagent using Bausch and Lomb spectronic 20 at 530 mμ. Standard curves for sodium and cobalt were prepared in the ranges of 0 to 5 ppm for sodium and 0 to 70 ppm for cobalt, vide figure 24, curves 1 and 2. The concentration of sodium per 100 gm of clay in equilibrium suspension and meq. of sodium left in the clay were then calculated. Similarly cobalt left in the equilibrium suspension in meq. per 100 gm clay and meq. of cobalt adsorbed per 100 gm clay were determined. The results are summarized in tables LXXXII to LXXXV.

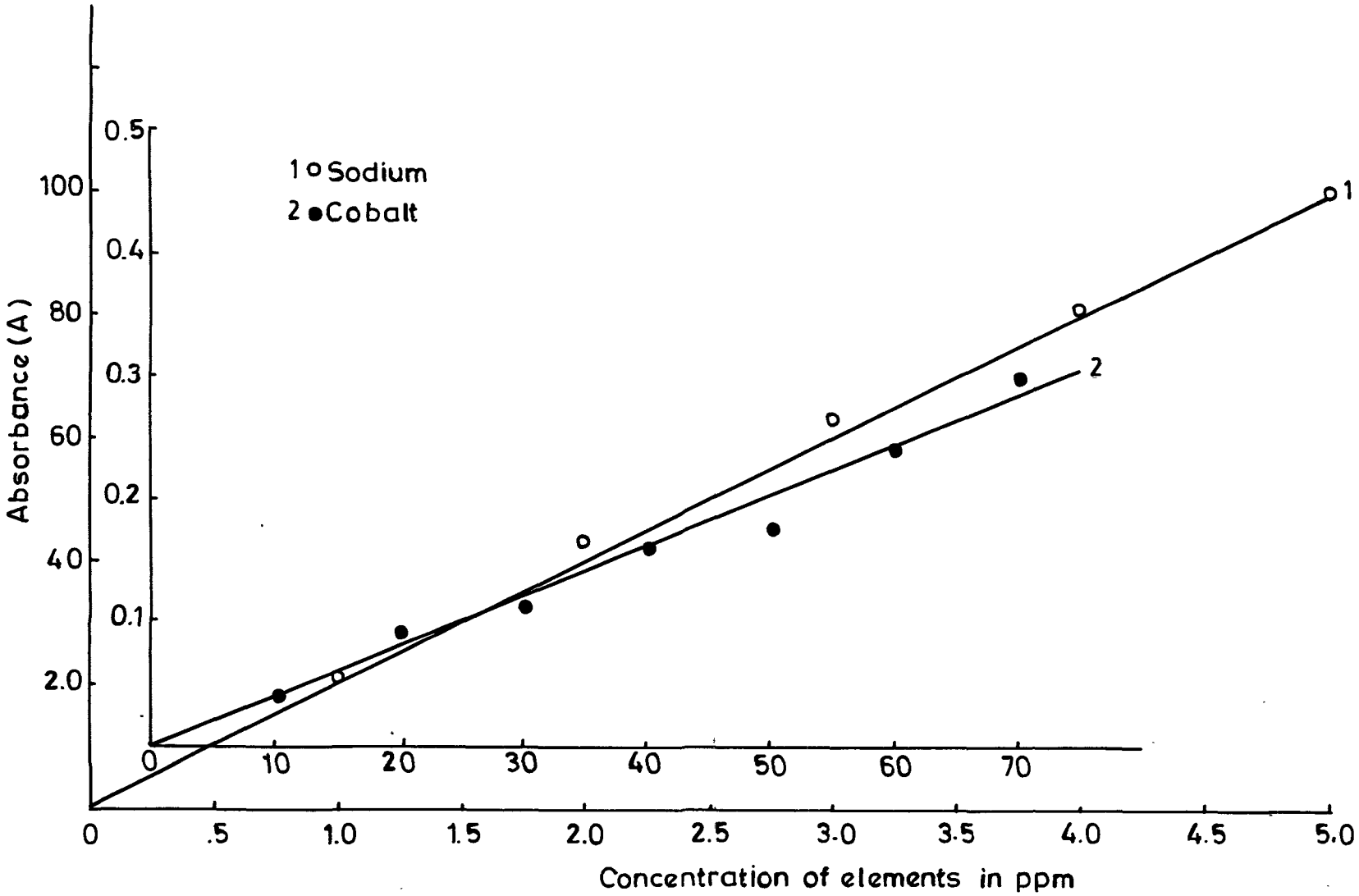

Fig. 24 Standard curves for Na and Co using flame photometer and spectrophotometric technique

Table LXXXII

Estimation of sodium by flame photometric method in the supernatant liquid of the montmorillonite suspension at 40° C.

Concentration of the clay = 0.0876 gms/10 ml

Volume of the suspension taken = 10.0 ml

Total volume of the suspension made = 25.0 ml

Flame photometer reading	Meq.of Na/100 gm clay in the equilibrium suspension	Meq. of Na in the clay
25.60	40.313	49.687
27.20	42.639	47.361
28.80	45.740	44.260
29.00	45.740	44.260
28.00	44.189	45.811
28.56	44.965	45.035
29.95	47.290	42.710
34.96	55.033	34.967
39.52	62.020	27.980
37.00	57.369	32.631

Table LXXXIII

Estimation of sodium by flame photometric method in the supernatent liquid of the montmorillonite suspension at 60°C.

Concentration of the clay = 0.0876 gms/10 ml

Volume of the suspension taken = 10.0 ml

Total volume of the suspension made = 25.0 ml

Flame photometer reading	Meq.of Na/100 gm clay in the equilibrium suspension	Meq. of Na in the clay
25.60	40.313	49.687
28.80	45.740	44.260
30.40	47.066	42.934
33.20	51.942	38.058
31.20	48.841	41.159
33.10	51.942	38.058
32.56	50.391	39.609
31.28	48.841	41.159
39.36	61.245	28.755
34.00	53.492	36.508

Table LXXXIV

Estimation of cobalt in supernatant liquid of montmorillonite suspension spectrophotometrically at 40°C.

Concentration of the clay = 0.0876 gm/10 ml

Volume of suspension taken = 10.0 ml

Total volume of the suspension made = 25.0 ml

Colour extracted with = Chloroform

Volume of $\frac{N}{250}$ cobalt nitrate added in ml	Meq. of cobalt added/100 gm clay	Cobalt left in the equilibrium suspension in meq/100 gm clay	Meq. of cobalt adsorbed/100 gm clay
6.0	27.396	2.442	24.954
7.0	31.962	3.715	28.247
8.0	36.528	5.262	31.266
9.0	41.094	7.739	33.355
10.0	45.660	8.050	37.610
11.0	50.226	10.080	40.146
12.0	54.792	11.580	43.212
13.0	59.358	8.900	50.458
14.0	63.924	8.917	55.007
15.0	68.490	13.160	55.330

Table LXXXV

Estimation of cobalt in supernatent liquid of montmorillonite suspension spectrophotometrically at 60°C

Concentration of the clay = 0.0876 gm/10 ml

Volume of the suspension taken = 10.0 ml

Volume of the suspension made = 25.0 ml

Colour extracted with = Chloroform

Volume of $\frac{N}{250}$ cobalt nitrate added in ml	Meq.of cobalt added/100 gm clay	Cobalt left in the equilibrium suspension in meq/100 gm clay	Meq.of cobalt adsorbed/100 gm clay
6.0	27.396	0.929	26.467
7.0	31.962	1.957	30.005
8.0	36.528	3.406	33.122
9.0	41.094	6.191	34.903
10.0	45.660	8.670	36.990
11.0	50.226	9.103	41.123
12.0	54.792	10.550	44.242
13.0	59.358	17.800	41.558
14.0	63.924	20.440	43.484
15.0	68.490	22.060	46.430

RESULTS AND DISCUSSION

The exchange reaction in the system can be written as:

$$\bar{C}_{Na} + C_{Co} \rightleftharpoons \bar{C}_{Co} + C_{Na} \qquad \ldots (1),$$

the equivalent cation ratios of cobalt in the clay and in solution being defined as

$$\bar{X}_{Co} = \frac{\bar{C}_{Co}}{\bar{C}_{o}} \quad \text{and} \quad X_{Co} = \frac{C_{Co}}{C_{o}} \qquad \ldots (2),$$

where C_{Co} and C_o are the equivalent concentration of cobalt in solution and the total electrolyte concentration respectively, $\bar{C}_{Co}$ and $\bar{C}_o$ are the equivalent concentration of cobalt and the total electrolyte concentration in the clay phase.[7] Similar notation has been adopted for sodium. These equilibrium results are shown in tables LXXXVI and LXXXVII. From

Table LXXXVI

Cobalt fraction in a clay as a function of its fraction in solution at 40° C

$\bar{X}_{Co}$	X_{Co}	CEC (Ca + Na) meq/g clay	$\bar{X}_{Na}$	X_{Na}
0.334	0.054	0.746	0.652	0.942
0.374	0.080	0.756	0.624	0.919
0.365	0.103	0.755	0.586	0.899
0.428	0.142	0.776	0.586	0.855
0.450	0.154	0.836	0.549	0.845
0.471	0.183	0.852	0.528	0.816
0.503	0.197	0.859	0.498	0.805
0.591	0.139	0.854	0.409	0.860
0.663	0.126	0.830	0.337	0.874
0.629	0.187	0.880	0.370	0.811

Table LXXXVII

Cobalt fraction in clay as a function of its fraction in solution at 60°C.

$\bar{X}_{Co}$	X_{Co}	CEC (Ca + Na), meq/g clay	$\bar{X}_{Na}$	X_{Na}
0.360	0.022	0.762	0.652	0.953
0.404	0.041	0.743	0.595	0.958
0.435	0.067	0.761	0.564	0.873
0.478	0.104	0.730	0.521	0.891
0.473	0.150	0.701	0.526	0.819
0.519	0.147	0.792	0.493	0.850
0.527	0.157	0.839	0.472	0.826
0.501	0.267	0.827	0.497	0.732
0.601	0.250	0.762	0.398	0.749
0.559	0.291	0.829	0.440	0.721

these results the exchange isotherms were drawn vide figure 25. From the figure it was quite clear that both at 40°C and 60°C cobalt(II) ions were preferably adsorbed by the clay. This appeared to be due to the higher charge on the cobalt(II) ions.

The selectivity quotient Kc was calculated from the formula

$$Kc = \left(\frac{\bar{X}_{Co}}{\bar{X}_{Na}}\right) \left(\frac{X_{Na}\,\gamma_{Na}}{X_{Co}\,\gamma_{Co}}\right) \qquad \ldots (3)$$

where γ was the ion activity coefficient. It was calculated by the Debye-Huckel[8] expression knowing the ionic strength and

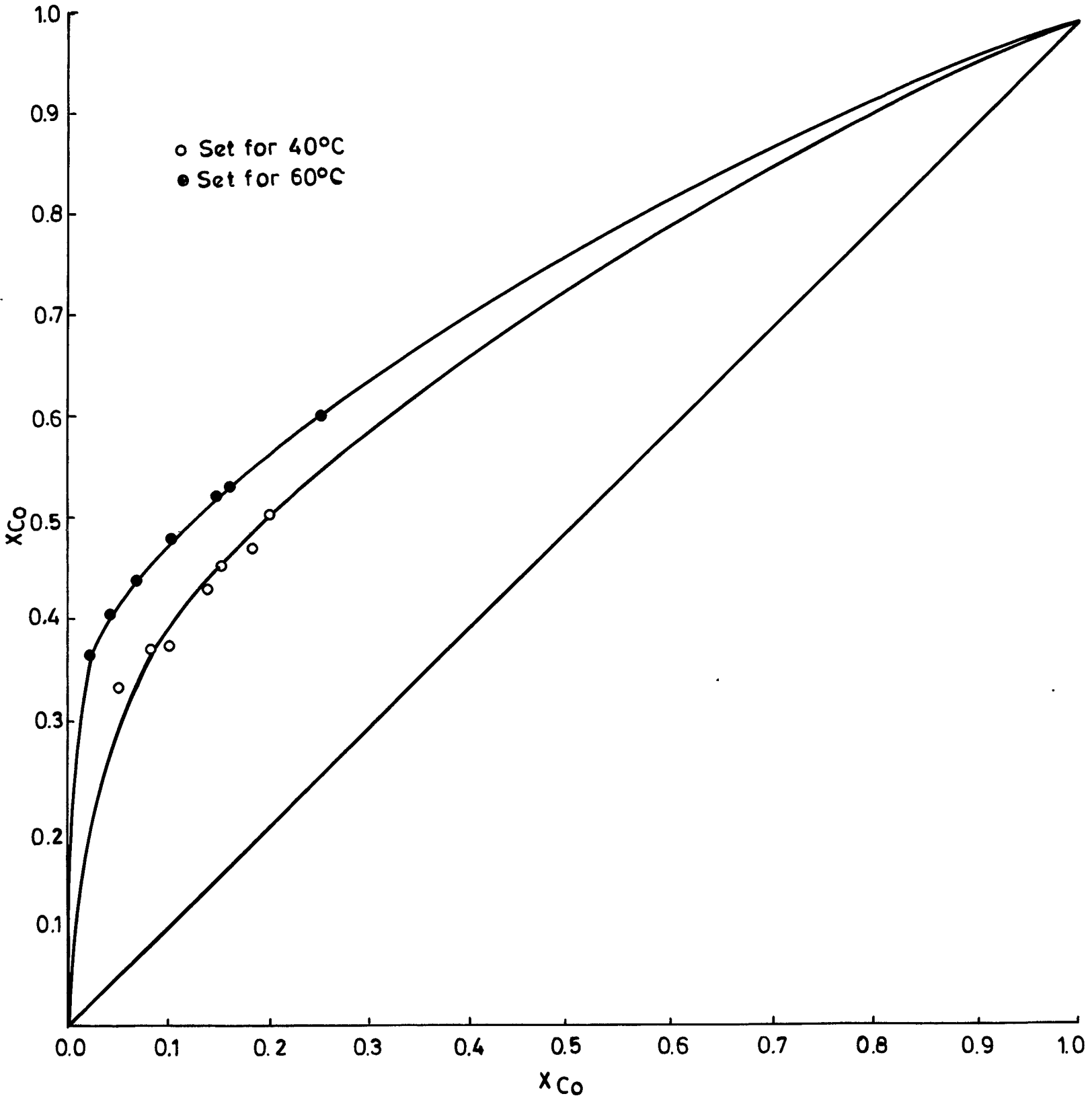

Fig. 25 Exchange isotherms for cobalt aquo ion

the molality of the solution. The thermodynamic exchange constant K was then calculated by:

$$\ln K = \int_0^1 \ln Kc \, d\bar{X}_{Co} \qquad \ldots (4)$$

The integral was evaluated graphically by plotting log Kc Vs. $\bar{X}_{Co}$ (Figure 26). The area under the curve was obtained by applying the trapezoidal rule.

The standard free energy ΔG° for reaction (1) was then calculated by

$$\Delta G^\circ = - RT \ln K \qquad \ldots (5)$$

and the standard enthalpy change ΔH° was obtained by the Van't Hoff equation to hold:

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = - \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ldots (6)$$

Finally, the standard entropy change ΔS° was calculated from the thermodynamic equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \qquad \ldots (7)$$

These thermodynamic quantities obtained for cobalt ion exchange

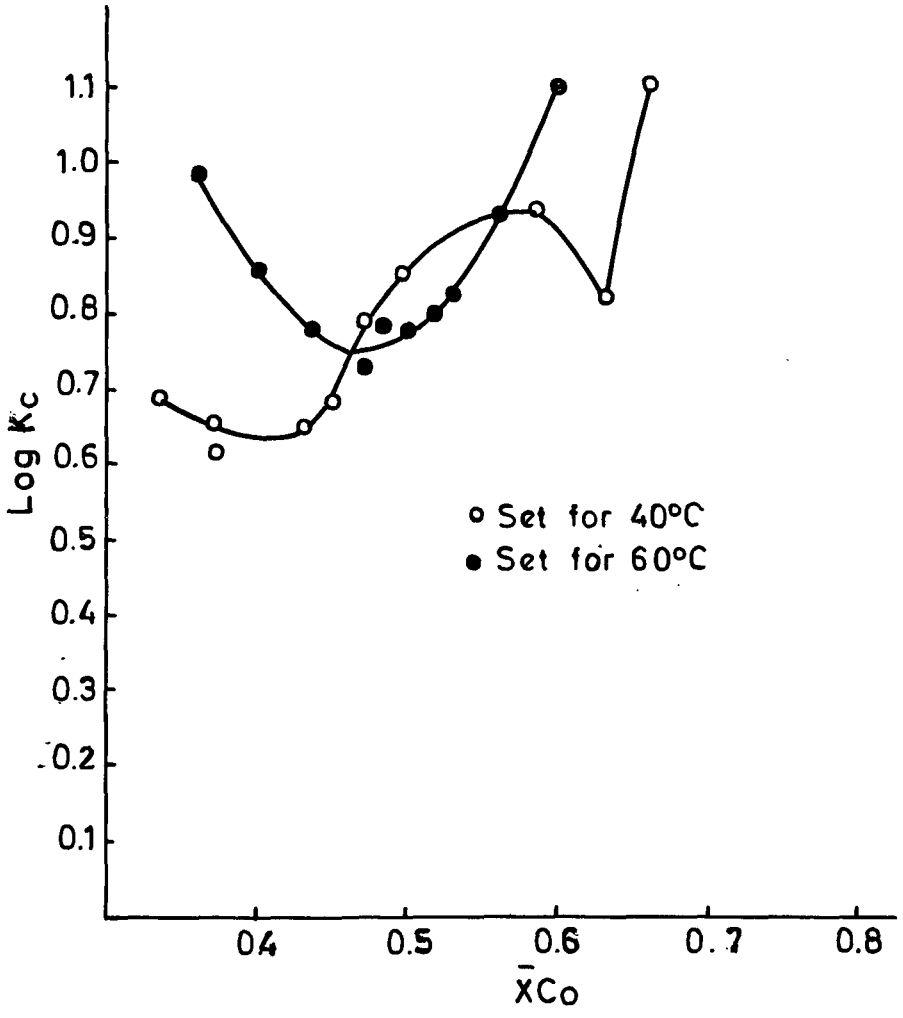

Fig. 26 Selectivity quotients as a function of cobalt fraction in clay

with sodium montmorillonite are summarized in table LXXXVIII.

Table LXXXVIII

Thermodynamic quantities for cobalt(II)-ion exchange with sodium montmorillonite.

Thermodynamic parameters	40°C	60°C
K	0.268	0.219
ΔG° (Cal/mole)	+ 154.6	+ 109.8
ΔH° (Cal/mole)	- 395.00	
ΔS° (Cal/degree mole)	- 1.30	

Decrease in enthalpy during the cobalt clay formation suggested that cobalt was most strongly bound with the clay. It was also supported by the exchange isotherms and also by the higher charge on cobalt. However, a positive free energy, pointed a stronger bond between the clay and sodium ions. But this was not conclusive because free energy was determined by enthalpy and entropy and binding strengths defined in terms of enthalpy alone. The entropy change was very small suggesting again thereby that the clay preferred Co^{+2} in comparison to Na^{+}.

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Nyomelemek eloszlása az Aligarh-i talajokban

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Az utolsó két évtizedben a nyomelemkutatás igen jelentőssé vált. Bebizonyosodott, hogy ezeknek az elemeknek fontos szerepe van a növények, valamint az állatok élettevékenységében és hogy akár a hiányuk, akár a túladagolásuk számottevően befolyásolja a növények termését, illetve az állatok egészségét. Az Uttar Pradeshben fekvő Aligarh körzet területe félmillió hektár, nagy földsávok mélyfekvésű, rossz drénviszonyú, gyengéntermő sós és alkálikus szikesek.

Az itt levő talajokat 6 típusba sorolták be [22]. Legtöbbnyire illittartalmúak, áteresztőképességük rossz, mechanikai összetételük és pH-juk különböző. Az időjárás aszályos és mérsékelten aszályos, az évi csapadék 500–600 mm. Az öntözés főképpen csőkutakból és csatornákból történik. A körzet főterményei a búza, bajra és jowar. A körzetnek a mezőgazdaság belterjesítési programjában játszott fontos szerepe miatt hasznosnak ítéltük a talajok szelvényében néhány nyomelem, így a bór, kobalt, réz és vas eloszlásának a vizsgálatát és e között, valamint a talajképző, illetve környezeti tényezők között az esetleges összefüggések kutatását.

Kísérleti rész

A talajok szelvénymintáit a körzet talajtérképe alapján [22] a reprezentatív területeken 182 cm mélységig gyűjtöttük be. A pH-t, valamint az elektromos vezetőképességet 1 : 5 arányú vizes szuszpenzióban, a talajok agyag- és mésztartalmát a szokásos módszerekkel mértük. A báziskicserélő képességet GANGULI módszerével [6] határoztuk meg. A bórtartalom mérése BERGER és TRUOG [2] szerint készített vizes kivonatban DIBLE és munkatársai [5] kolorimetrikus módszerével kurkumin-oxálsavas reagens segítségével 550 mμ-nél történt. Az összes kobalt tartalmat perklórsavas kezelés után 1 nitrozo-2-naftollal képezett szín alapján [18] határoztuk meg. Az összes-, valamint felvehető réztartalmának a vizsgálata CHENG és BRAY [3] karbamátos eljárásával történt, az összes rezet a perklórsavas feltárás után [8], a felvehető rezet semleges ammónium citrátos kivonatban határoztuk meg. Az összes vas kivonása savanyú (3-as pH-jú) normál ammónium acetát oldattal történt, kolorimetrikus meghatározása pedig o-fenantrolin reagenssel [19].

Az eredményeket az 1. táblázatban foglaltuk össze.

1. táblázat

Az Aligarh-i körzet talajainak fiziko-kémiai tulajdonságai

(1) Típus	(2) Mélység cm	(3) Elektromos vezetőképesség mmhos/cm	pH	(4) T érték mgeé./100 g	$CaCO_3$ %
I	0— 28	0,2270	8,47	2,38	10,75
	28— 38	0,1575	8,10	1,59	10,133
	38— 43	0,1827	8,22	1,67	10,88
	43— 48	0,1731	8,12	1,67	9,64
	48— 91	0,1289	8,10	0,40	0,50
II	0— 18	0,1644	7,60	13,96	5,14
	18— 36	0,1289	7,95	11,50	5,76
	36— 58	0,1196	8,00	10,31	4,93
	58— 79	0,1241	8,10	12,37	4,50
	79— 97	0,1115	7,65	11,10	4,13
	97—127	0,1230	7,85	26,01	4,01
	127—168	0,1061	7,50	26,33	3,88
III	0— 30	0,4699	9,35	20,62	8,16
	30— 61	3,2801	9,80	14,90	10,43
	61— 81	1,3100	8,72	5,00	45,64
	81—114	1,9100	8,65	1,98	51,13
	114—137	0,2860	8,37	1,90	53,76
	137—152	0,1879	7,37	2,06	15,25
	152—182	0,1686	7,50	1,11	14,63
IV	0— 28	0,1174	8,15	9,86	8,01
	28— 63	0,1134	7,60	9,99	6,00
	63— 96	0,5982	8,07	2,21	4,88
	96—135	0,5487	8,55	13,54	4,50
	135—182	0,6578	8,52	14,75	4,38
V	0— 28	0,4385	8,85	3,25	9,00
	28— 58	0,6578	9,95	3,33	10,01
	58— 94	0,0109	9,65	5,53	10,26
	94—112	0,0082	9,50	4,40	9,25
VI	0— 30	0,0657	8,00	15,46	6,65
	30— 58	0,0597	7,95	22,28	3,88
	58— 92	0,5296	8,45	4,92	20,05
	92—147	0,2990	8,45	4,72	25,93

Az eredmények értékelése

Az 1. táblázatban a 6 szelvény pH, elektromosvezetőképesség, valamint kalciumkarbonát-tartalmának adatai szerint az Aligarh talajok többnyire sós és meszes szikesek. A III., V. és VI. szelvényben lefelé a $CaCO_3$-tartalom növekszik, míg az I., II. és IV. szelvényben csökken. Különösen meszes és elszikesedett a III. szelvénnyel jellemezett talajtípus. A talaj valószínűleg meszes allúviumon alakult ki, ez okozza nagy mésztartalmát. A talajok fizikai sajátosságaik szerint agyagtól homokos vályogig váltakozóak.

A 2. táblázatban látható, hogy a talajok vízben oldható bórtartalma 0,60—11,48 mg/kg között váltakozik, az átlagos érték a körzetben 4,5 mg/kg.

2. táblázat

Az Aligarh-i talajok nyomelem tartalma, mg/l kg talaj

(1) Típus	(2) Vízben oldható B	(3) Összes Co	(4) Cu		(5) Összes Fe
			Összes	Felvehető	
I	6,92	16,00	48,81	1,00	74,00
	6,90	15,00	48,62	0,50	100,00
	6,80	12,50	48,60	1,00	96,00
	5,28	10,00	48,58	0,00	110,00
	3,68	0,00	34,87	0,00	117,00
II	2,80	3,00	33,59	1,00	5,00
	3,20	4,00	56,74	1,45	48,00
	2,40	3,50	45,43	1,00	32,00
	1,28	3,00	53,36	1,20	6,00
	0,60	1,50	40,15	1,20	98,00
	1,16	10,00	54,56	0,50	62 00
	1,60	61,50	57,55	2,25	37,00
III	3,64	32,50	47,51	1,00	86,00
	3,48	33,50	42,09	0,75	64,00
	7,36	34,00	55,09	0,50	60,00
	5,76	15,00	50,61	2,30	88,00
	9,92	19,00	47,06	1,25	90,00
	9,60	22,00	36,26	1,20	40,00
	7,20	25,00	31,97	1,00	20,00
IV	6,48	12,50	53,89	1,45	35,00
	11,48	18,50	57,35	1,45	28,00
	8,18	20,00	53,72	1,00	14,00
	4,52	19,00	58,88	4,50	84,00
	2,64	5,00	50,43	1,25	22,00
V	2,64	10,00	45,15	2,25	110,00
	3,52	15,00	58,61	0,25	16,00
	2,00	31,00	47,57	0,50	9,00
	5,20	25,00	50,86	1,00	92,00
VI	1,84	42,00	47,91	0,25	12,00
	2,40	53,00	50,67	0,50	62,00
	2,80	50,00	60,01	0,25	20,00
	1,76	64,00	49,92	0,50	96,00

REEVES és munkatársai szerint vízben oldható bórtartalomban a normális és a hiányos ellátottságú talajok között 0,35 mg/kg a határérték, míg RICHARDS [4] szerint 0,70 mg/kg alatti értékek még a bórra érzékeny növényekre sem károsak, 0,70—1,05 mg/kg között van az átmenet, míg 1,50 mg/kg-nál nagyobb B-töménységek már károsak lehetnek. Ezt az osztályozást elfogadva a vizsgált talajokban a vízben oldható bór értéke inkább a magasabb határértékhez van közelebb.

Az egyes talajtípusok vidékéről a kutakból vett vízminták elemzési eredményei a 3. táblázatban láthatók. Valószínűleg a vizeknek gyakran a biztonságos szintnél is nagyobb bórtartalma a forrása a talajok bórgazdagságának. Különösen nagy a bórtartalma az I., III., és IV. szelvényeknek. Érdekes, hogy éppen ezeknek a szelvényeknek kicsi az áteresztőképessége. Az I. és IV. szelvényben szemben, a többivel, lefelé általában csökken a talaj bórtartalma.

3. táblázat

Az öntözővizek nyomelemtartalma különböző talajtípusokon

(1) Talajtípus	(2) Mikroelemek				(4) Összes Fe
	B	Co	(3) Cu		
			Összes	Felvehető	
I	0,042	0,00	nil	nil	nil
II	0,025	0,00	nil	nil	nil
III	0,025	0,00	nil	nil	nil
IV	0,030	0,005	nil	nil	nil
V	0,050	0,00	nil	nil	nil
VI	0,063	0,00	nil	nil	nil

A talajok pH-ja és B-tartalma között nem volt összefüggés ($r = -0{,}0001$), ahogy ezt PALIWAL és ANJANEYULU [15] Delhi-i, valamint MATHUR és munkatársai [11] nem öntözött Rajastan-i talajokon megfigyelték, ugyanakkor ellentétben KANWAR és SINGH [20] észleléseivel. Nem találtunk összefüggést a talajok elektromos vezetőképessége és bórtartalma között sem ($r = -0{,}002$). A bórtartalomnak változása a várakozásnak megfelelően szignifikáns negatív összefüggésben van a kationkicserélő képességgel ($r = -0{,}41$), a vízben oldható bórtartalom, valamint a $CaCO_3$-tartalom között viszont szignifikáns pozitív összefüggést találtunk. Ez összhangban van MATHUR-ék már idézett rajasthani vizsgálataival. Lehetséges,hogy a kalciumkarbonát az Aligarh-i talajszelvényekben a bór nagymértékű felhalmozódását előidéző másik tényező. GREWAL és munkatársai [7] viszont a talajok felvehető bórtartalma és kalciumkarbonát-tartalma között nem találtak szignifikáns összefüggést. Ezeknek a talajoknak a nagy bórtartalma felveti az érzékeny növények bórmérgezés ellen való megvédésének a problémáját, a mérgezésnek a tünetei, mint a törpeség, a levelek perzselődése gyakran láthatók a körzet növényein. Úgy találták azonban, hogy a félig ellenálló növények, mint a búza vagy az árpa, a bórártalmat elviselik.

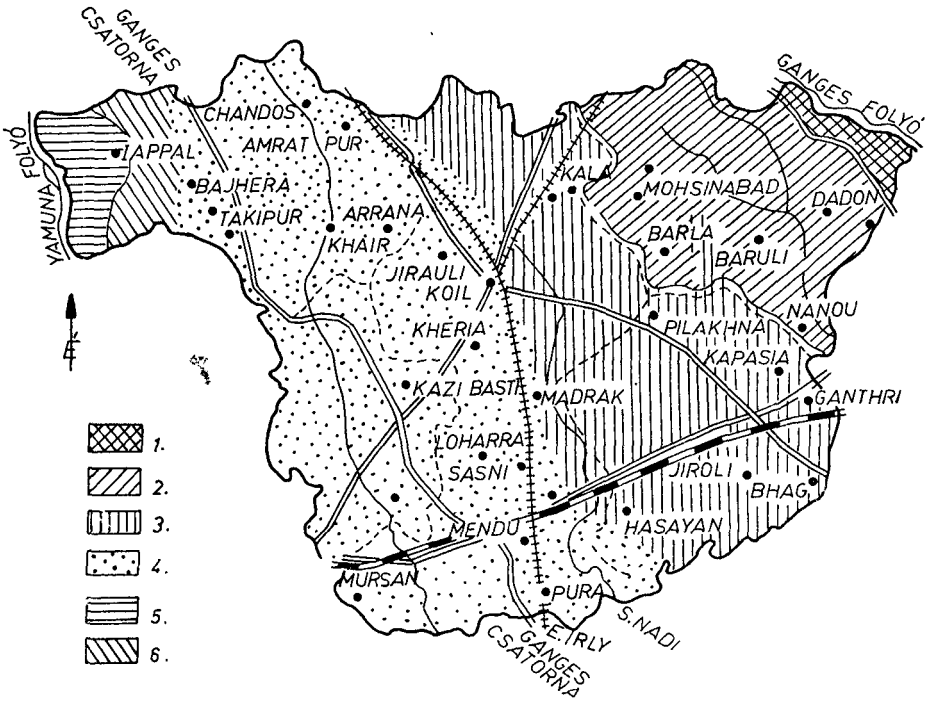
A talajok összes kobalt-tartalma valamennyi szelvényre 3—64 mg/kg talaj között változik, az átlag 21,21 mg/kg. A felszínmenti rétegből vett minták esetében a szélső értékek 3 és 42 mg/kg, az átlag pedig 19,33 mg/kg. SINGH és SINGH [21] Uttar Pradesh-i talajokban 4,6—29,1 mg/kg közötti összes kobalt tartalmakat találtak. WALSH és munkatársai szerint 2,5 mg/kg-on aluli kobalttartalmak a növény növekedése, valamint az állatok táplálkozása szempontjából már erős hiányt jelentenek, 2,5 és 5 mg/kg közötti tartalmak esetében a hiány mérsékelt, míg 5,0 mg/kg felett a kobaltellátottság kielégítő. A talajok kobalt szintje, tehát jelentősen a hiányos állapot felett van, és a körzetben termesztett növények számára nincs kobaltadagolásra szükség. Az I. szelvényt kivéve, ahol lefelé az összes kobalttartalom csökken, a mélységbeni eloszlásban semmi különösebb szabályszerűséget nem találtunk. A II., V. és VI. szelvény mélyebb szintjeiben, valamint az I. és III. szelvény legfelső szintjében nagymérvű kobalt felhalmozódás tapasztalható. Történetesen az I. és III. szelvények átjárhatósága csekély. A kobalt és a talajtulajdonságok közötti összefüggéseket vizsgálva (4. táblázat) megállapítható, hogy az összes kobalttartalom szignifikáns korrelációban van a talaj kalciumkarbonáttartal-

4. táblázat

A talajok fiziko-kémiai tulajdonságai és az egyes nyomelemek koncentrációja közötti korrelációk együtthatói

(1) Nyomelem	(2) Elektromos vezetőképesség mmhos/cm	pH	(3) T érték mgeé./100 g	$CaCO_3$ %
a) Vízoldható bór	—0,002	0,000	—0,410	0,350
b) Összes Co	—0,012	0,000	0,680	0,450
c) Összes Cu	—0,045	—0,080	0,510	0,090
d) Felvehető Cu	0,009	—0,150	0,790	0,024
e) Összes vas	—0,050	0,044	—0,260	0,180

mával, valamint kationkicserélő képességével, míg a pH-val és az elektromos vezetőképességgel nem mutat ilyen összefüggést. Az eredmények a kalciumkarbonát vonatkozásában BODDIE, a pH vonatkozásában pedig REDDY és MEHTA [17] megfigyeléseivel összevágnak, míg SINGH és SINGH [21] észleléseivel ellenkeznek. A 3. táblázatban látható öntözővíz elemzéseket figyelembe véve megállapítható, hogy a talajok kobaltellátása nincs az öntözővízzel összefüggésben.



1. ábra

Aligarh talajtérképe, 1. Ganga vályogos homok. Aligarh körzet; 2. vályog, 3. agyagos vályog, 4. homokos vályog. Yamuna vidéke: 5. iszapos agyagos vályog, 6. homokos vályog.

Az összes réztartalom valamennyi szelvényminta átlagában 48,87 mg/kg (a szélső értékek 31,00—62,01) a legfelső szint mintáiban pedig átlagosan 46,14 mg/kg (33,59—48,81). A felvehető réztartalomra a megfelelő értékek 1,07 (0—4,50), illetve 1,17 (0,25—2,25). A 2. táblázatban az is látható, hogy az összes réztartalomnak átlagosan csak mintegy 2%-a felvehető. Ennek oka az lehet, hogy nincs a talajokban egy olyan oldható anyag, amely a rezet komplex kötésbe vinné. A növények rézszükséglete termesztett növényenként más és más. LUNDBALD és munkatársai [10] az összes réztartalom határértékét 7,0 mg/kg-nál vonták meg, míg PIPER [16] a felvehető réztartalom határértékére 0,5 mg/kg-t javasolja. Ezeket figyelembe véve összes rézben egyik talajunk sem szenved hiányt, míg felvehető rézben talajaink 15%-a nem felel meg a követelményeknek. Ezek az I. és II. típushoz tartozó talajok ún. „khadar" vidéken vannak. A réztartalom szignifikáns korrelációban volt a talaj kationkicserélő képességével (felvehető rézre a $r = 0{,}510$, míg az összes réztartalomra $r = 0{,}788$), míg nem volt kimutatható korrelációjuk a talaj pH-jával, elektromos vezetőképességével és %-s kalciumkarbonát tartalmával. A különböző szerzők [1, 9, 12, 13, 14] a talajok felvehető réztartalmát befolyásoló tényezőket tanulmányozva ellentmondó eredményeket kaptak és így nem lehet végleges megállapítást tenni a talaj felvehető réztartalma és fizikokémiai tulajdonságai között. A „khadar" vidékeken a szervestrágyákkal együtt adott réznek a termesztett növényeknél kedvező hatását tapasztalhatjuk.

A talajok összes vastartalma igen változó. A szelvényből vett valamennyi minta átlagában a vastartalom 57,28 mg/kg volt (szélsőértékek 5 és 117), míg a legfelső szintből vett mintákban 53,66. Ezekben a mintákban a tárolás során bekövetkező oxidáció miatt a ferro alakban levő vastartalmat pontosan nem állapíthatjuk meg. Az előkísérletek szerint az összes vas jelentős része ferri alakban, illetve csapadék formájában van és így a növények számára nem felvehető. A vastartalom, valamint a talaj fiziko-kémiai tulajdonságai közötti korrelációt vizsgálva megállapítható, hogy az egyes változók és a vastartalom között 5%-os valószínűségi szinten nincs korreláció, bár lehet, hogy összességükben a talaj vasszintjét meghatározzák. Ez egybevág azoknak a szerzőknek a megállapításaival, akik Punjab-i talajokon a vastartalomban nem találtak következetességet.

A szerzők köszönetet mondanak Siraj Mohd Khan-nak, a statisztikai számítások elvégzéséért.

Összefoglalás

Az Aligarh-i körzet néhány jellegzetes talajszelvényében a mikrotápanyag tartalmat vizsgáltuk. A vízbenoldható bór, a kobalt és az összes réz mennyisége jóval a körzetben termesztett növények szükségletei felett volt, és így ezeknek nincs szükségük az említett elemek adagolására. A „khadar" talajtípusok néhány szintje azonban felvehető rézben szegény, és ezekben indokolt a rezet komplexbevivő szerek alkalmazása.

Szignifikáns pozitív korrelációt találtunk a vízben oldható bór, valamint kalciumkarbonát-tartalom között, a kobalttartalom és a kationkicserélőképesség valamint a kalciumkarbonát-tartalom között, illetőleg az összes és felvehető réz, valamint a kationkicserélő képesség között. Ugyanezzel a bórtartalom negatív korrelációban van. A pH-val, valamint az elektromos vezetőképességgel a mik-

roelemek mennyisége nem mutatott szignifikáns korrelációt. A talajokban, mint heterogén rendszerekben a különböző változók együttes hatása befolyásolja, minden bizonnyal, a vizsgált mikrotápelemek felvehetőségét.

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Distribution of Trace Elements in Aligarh Soils

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Summary

The micronutrient status of some typical soil profiles of Aligarh district has been examined. It has been noticed that the water soluble boron, cobalt and total copper are well over the deficiency limit in the soils and no application of these nutrients is necessary for managing the crops of the district. Available copper, however, shows deficiency in some layers of 'khadar' soil types I and VI and application of complex agents that can release copper is suggested.

Significant positive correlations between water soluble boron and calcium carbonate content, cobalt and cation exchange capacity as well as calcium carbonate, total and available copper and cation exchange capacity have been observed. Boron exhibits a negative correlation with cation exchange capacity. The values of correlation coefficients between the quantity of micronutrients and pH and electrical conductivity are insignificant. An integrated effect of the various variables seems to effect the availability of these nutrients to crops on these heterogeneous soil systems.

Table 1. Physico-chemical characteristics of the soils of Aligarh district. (1) Type. (2) Depth in cm. (3) Electric conductivity mmhos/cm. (4) C. E. C. me./100 mg soils.

Table 2. Trace element status of Aligarh soils, mg/1 kg soil. (1) Type. (2) Water soluble boron. (3) Total cobalt. Total and available Copper. (4) Total iron.

Table 3. Trace element status of the irrigation water of different soil types. (1) Soil type. (2) Micronutrients. (3) Total and available copper. (4) Total iron.

Table 4. Correlation coefficients between physicochemical properties of the soil and the trace elements. (1) Micronutrients: *a)* Water soolble boron. *b)* Total Co. *c)* Total Cu. *d)* availbale Cu. *e)* Total iron. (2) Electric conductivity, mmhos/cm. (3) C. E. C. me/100 g.

Figure 1. Aligarh district. (1) Ganga loamy sand. (2) Aligarh loam. (3) Aligarh clay loam. (4) Aligarh sandy loam. (5) Yamuna silty clay loam. (6) Yamuna sandy loam.

Die Mikronährstoffverteilung in Böden des Kreises Aligarh

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Zusammenfassung

In einigen charakteristischen Bodenprofilen des Kreises Aligarh wurde der Mikronährstoffgehalt bestimmt. Die Menge des Bors, Kobalts, sowie des gesamten Kupfers lag bedeutend über dem Bedarf der hier üblichen Pflanzen, diese Elemente müssen also in Form von Düngern nicht gegeben werden. Einige Horizonte der „khadar"-Bodentypen sind aber an aufnehmbarem Kupfer arm, in diesen Fällen ist die Zugabe von Kupferkomplex-Düngermitteln begründet.

Zwischen dem wasserlöslichen Bor- und $CaCO_3$-Gehalt, dem Kobaltgehalt und der Kationenaustauschkapazität einerseits und dem $CaCO_3$-Gehalt andrerseits, bzw. zwischen der gesamten und aufnehmbaren Cu-Menge und der Kationenaustauschkapazität konnte eine signifikante positive Korrelation festgestellt werden. Der Borgehalt zeigte mit der Kationenaustauschkapazität eine negative Korrelation. Die Menge der Mikronährstoffe zeigte keine signifikante Korrelation mit dem pH-Wert und der elektrischen Leitungsfähigkeit. Die Aufnehmbarkeit der untersuchten Mikronährstoffe wird in den Böden, welche als heterogene Systeme betrachtet werden müssen, aller Wahrscheinlichkeit nach durch die gemeinsame Wirkung der verschiedenen Faktoren bestimmt.

Tab. 1. Physikalisch-chemische Eigenschaften der Böden im Kreise Aligarh. (1) Bodentyp. (2) Tiefe in cm. (3) Elektrische Leitungsfähigkeit, mmhos/cm. (4) T-Wert, mamvol./100 g.

Tab. 2. Mikronährstoffgehalt der Böden des Kreises Aligarh, mg/1 kg Boden. (1) Bodentyp. (2) Wasserlösliches Bor. (3) Gesamtes Co. (4) Gesamtes und aufnehmbares Cu. (5) Gesamtes Eisen.

Tab. 3. Mikronährstoffgehalt des Bewässerungswassers auf verschiedenen Bodentypen. (1) Bodentyp. (2) Mikronährstoffe. (3) Gesamtes Eisen.

Tab. 4. Korrelationskoeffizienten zwischen den physikalisch-chemischen Eigenschaften der Böden und der Konzentration einiger Mikronährstoffe. (1) Mikronährstoff. (2) Elektrische Leitungsfähigkeit, mmhos/cm. (3) T-Wert, mval /100 g.

Abb. 1. Bodenkarte von Aligarh. 1. Ganga, lehmiger Sand. Kreis Aligarh: 2. Lehm. 3. toniger Lehm. 4. sandiger Lehm. Gegend von Yamuna: 5. schlammiger toniger Lehm. 6. sandiger Lehm.

Изучение распределения микроэлементов в некоторых характерных почвах провинции Алигарх

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Резюме

В некоторых, характерных для провинции Алигарх, почвенных разрезах определялось содержание микроэлементов. Содержание в почвах водорастворимого бора, кобальта и общей меди превышала потребность в них растений, выращиваемых на этой территории, поэтому нет надобности вносить в почву вышеназванные микроэлементы. Некоторые горизонты почв «кхадар» бедны медью, поэтому здесь обосновано внесение в почву соединений меди.

Отмечена положительная достоверная корреляция между содержанием водорастворимого бора и карбонатов кальция, между содержанием кобальта и характером катионного обмена, а также содержанием карбонатов кальция, кроме того между содержанием общей и усвояемой меди и характером катионного обмена. Содержание бора находится в отрицательной зависимости со всеми вышеперечисленными свойствами.

Не наблюдалось достоверной зависимости между количеством микроэлементов, pH и электропроводностью.

В почвах, как в гетерогенных системах, по всей вероятности усвояемость изучаемых микроэлементов изменяется под влиянием совместного действия различных изменяющихся факторов.

Табл. 1. Физико-химические свойства почв в районе Алигарха. (1) Тип. (2) Глубина в см. (3) Электропроводность м. ом · $см^{-1}$. (4) Величина «Т» в мг. экв/100 г.

Табл. 2. Содержание микроэлементов в почвах района Алигарх в мг/1 кг почвы. (1) Тип. (2) Водорастворимый бор. (3) Общий кобальт. (4) Общая и усвояемая медь. (5) Общее железо.

Табл. 3. Содержание микроэлементов в поливных водах на различных почвенных типах. (1) Тип почвы. (2) Микроэлементы. (3) Общее железо.

Табл. 4. Корреляционные коэффициенты зависимости между физико-химическими свойствами почв и концентрациями отдельных микроэлементов. (1) Микроэлемент. (2) Электропроводность в м·ом. $см^{-1}$. (3) Величина «Т» в мг. экв/100 г.

Рис. 1. Почвенная карта провинции Алигарх. 1. Ганга; супесь. Район Алигарха: 2. Суглинок. 3. Тяжелый суглинок. 4. Легкий суглинок. Район Ямуна: 5. Иловатый тяжелый суглинок. 6. Супесь.

Öntözővizek és műtrágyák bórtartalmának hatása a termesztett növényekre a Chambal-vidékén

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A bór egyike azoknak a mikroelemeknek, amelyre az utóbbi évtizedekben nagy figyelmet fordítottak. Fontosságának az az oka, hogy az egyes termesztett növények optimális növekedéséhez elengedhetetlenül fontos, másrészt azonban már kis feleslegben is a levelek elhalását, perzselődését és még más rendellenességeket okoz a növényekben.

SCHOFIELD (1935), WILCOX (1949) és még néhányan úgy találták, hogy a talajok bórtartalma 1,25 mg/kg felett a legtöbb érzékeny növényre káros, 1,25—2,5 mg/kg között a közepesen érzékeny növényekre is mérgező, míg 2,5 mg/kg felett már a legtöbb termesztett növényt bórtűrésük szerint többékevésbé károsítja. EATON [5] ezzel szemben hangsúlyozta, hogy az egyes növényfajok bórigénye és bórtűrése igen különböző.

Az egyes termesztett növényfajok különböző klímaviszonyok közötti bórtűréséről, azaz a bór toxikusságának a határértékéről, még ma sincsenek pontos adataink. Munkánkban a Chambal-vidéken termesztett néhány növényfaj, az öntözővíz és az általánosan használt műtrágyák bórtartalmával foglalkozunk.

Anyagok és módszerek

A művelt talajok, kutak és csatornák öntözővize és néhány termesztett növényfaj mintáit a Chambal-vidék különböző helységeiben a monszun előtti, illetve utáni talajtérképezés során gyűjtöttük. A talajmintákat a megművelt táblákon 0—22,5 cm rétegből vettük. Vizsgálat előtt a talajmintákat levegőn megszárítottuk. A vízmintákat néhány, a talajmintavétel közelében levő kútból gyűjtöttük. Ezenkívül a különböző évszakokban a körzetben termesztett egyszikű és kétszikű növényeket is megmintáztuk. A növénymintákat desztillált vízben megmostuk, felapróztuk, 105 C fokon 24 órán át szárítottuk, majd külön-külön az elemzéshez elporítottuk.

A talajminták és vízminták pH-ját elektromosan, a szerves széntartalmat pedig Walkley és Black módszerével határoztuk meg. A vízminták, valamint a talajminták és műtrágyák felvehető bórtartalmának meghatározása a RICHARDS-féle [4] karmin módszerrel történt. A növények bórtartalmát JACKSON [8] előírása szerint savas extraktban karmin módszerrel állapítottuk meg.

Eredmények és azok megbeszélése

Az első táblázatban a kutakból és csatornákból származó öntözővizek és a Chambal-terület megművelt talajainak pH-ja, szerves szén- és bórtartalma